

(51) International Patent Classification ⁶ : C10L 1/14, 10/00	A1	(11) International Publication Number: WO 95/33022	(43) International Publication Date: 7 December 1995 (07.12.95)
(21) International Application Number: PCT/US95/06758 (22) International Filing Date: 31 May 1995 (31.05.95) (30) Priority Data: <div style="display: flex; justify-content: space-between;"> <div>251,723</div> <div>31 May 1994 (31.05.94)</div> <div>US</div> </div> <div style="display: flex; justify-content: space-between;"> <div>419,464</div> <div>10 April 1995 (10.04.95)</div> <div>US</div> </div> (71)(72) Applicant and Inventor: ORR, William, C. [US/US]; 2075 South University #240, Denver, CO 80210 (US). (74) Agents: KOVARIK, Joseph, E. et al.; Sheridan, Ross & McIntosh, Suite 3500, 1700 Lincoln Street, Denver, CO 80203 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i>	

COMBUSTION TEMPERATURE DIFFERENCES

(TEST TWO)

Y-axis: EXHAUST ENGINE GAS TEMPERATURE (EGT °f)
X-axis: LOAD (ihp)

Legend:

- B - BASE FUEL
- M - MANGANESE FUEL
- O - MTBE FUEL
- - DMC FUEL
- △ - METHYLAL FUEL
- - MEOH FUEL

Key Data Points and Annotations:

- At 20 ihp, Base Fuel EGT is 828°f, while Manganese Fuel EGT is 850°f.
- At 15 ihp, Manganese Fuel EGT is 745°f.
- At 20 ihp, Manganese Fuel EGT is 769°f.
- At 22 ihp, Manganese Fuel EGT is 756°f.
- At 24 ihp, Manganese Fuel EGT is 780°f.
- At 24 ihp, Base Fuel EGT is 780°f.
- At 24 ihp, MEOH Fuel EGT is 780°f.
- At 24 ihp, Methylal Fuel EGT is 780°f.
- At 24 ihp, DMC Fuel EGT is 780°f.
- At 24 ihp, MTBE Fuel EGT is 780°f.
- At 24 ihp, Base Fuel EGT is 780°f.

Comparison at 20 ihp:

- Base Fuel EGT: 828°f
- Manganese Fuel EGT: 850°f
- Difference: 22°f

Comparison at 24 ihp:

- Base Fuel EGT: 780°f
- Manganese Fuel EGT: 780°f
- Difference: 0°f

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VAPOR PHASE COMBUSTION METHODS AND COMPOSITIONS**BACKGROUND OF THE INVENTION****Field of the Invention**

5 This invention relates to methods and fuel compositions capable of vapor phase combustion for use in jet, turbine, diesel, fuel oil, gasoline and other combustion systems. More particularly, it relates to metallic vapor phase fuel combinations with high heats of
10 enthalpy capable of major free energy improvements while simultaneously reducing combustion temperature.

Description of the Prior Art

 The incorporation of metallics, including various
15 organo-manganese compounds as anti-knock agents (e.g. methylcyclopentadienyl manganese tricarbonyl -MMT, et al.) in hydrocarbon fuels, is known. See U.S. Patents 2,818,417; 2,839,552; and 3,127,351 (incorporated herein by reference). Organo-manganese's use in heavier fuels such
20 as coal, diesel and jet aviation fuels is also known and believed to help reduce smoke and solid particulate emissions. See U.S. Patents # 3,927,992; 4,240,802; 4,207,078; 4,240,801.

 Despite organo-manganese's anti-knock and other
25 benefits, its use in hydrocarbon fuels produces another set of environmental and practical problems. Namely, metallic based fuels form metallic oxides in combustion. In the case of organo-manganese compounds, such metallics when combusted in hydrocarbon fuels generate harmful heavy

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manganese oxides (Mn_3O_4 and Mn_2O_3), which in turn coat engine parts, combustion systems, turbines, exhaust surfaces, emission/exhaust catalysts, etc., causing for example, early fatigue, failure, excessive wear, particulate emissions of metals, long term hydrocarbon emission degradation, and the like. See U.S. Patents 3,585,012; 3,442,631; 3,718,444; and my EPO Patent # 0235280.

Harmful metallic deposition is well known and heretofore the practical problem in metallic usage. For example, deposition of manganese oxide on jet engines, turbines, and the like, has long been a major obstacle to manganese's use. Due to the severity of manganese deposits, various methods were developed just to remove such oxides from jet engines. See U.S. Patent 3,556,846; 3,442,631; 3,526,545; 3,506,488. Unfortunately, due to the magnitude of this disability, metallic usage has been virtually halted in such applications, and alternative application is limited to very low concentrations of metallic.

U.S. Patent 4,600,408 (issued in 1986) discloses an alkyl phenyl carbonate as an anti-knock agent. Patent 4,600,408 notes the aforementioned organo-manganese oxide problem and discloses its composition must be organo-manganese free.

Since those skilled in the art have long since abandoned hopes of solving the fundamental oxide disability of metallic combustion, and given that manganese is illegal in unleaded gasolines, practitioners have long been disinclined to separate MMT from lead additive usage. See

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for example, European Patent Application 91306278.2 related to "Unsymmetrical dialkyl carbonate fuel additives," which recognizes this reality by disclosing tetraethyl lead, tetramethyl lead and cyclopentadienyl tricarbonyl manganese together in the same context, absent suggestion of employing them independently of each other.

Summary of Invention

Applicant has discovered a new class of high energy cool combustion compositions and processes, which is additionally taught in companion Application # PCT/US95/02691, filed 3/2/95 and incorporated by reference in all regards to instant claimed invention.

The essence of Applicant's invention resides in the discovery of the source of heavy metal oxidation problem, which occurs in a less than ideal combustion process wherein combustion burning velocities and temperatures are not optimized.

By effectively increasing the burning velocity of the fuel, while ideally reducing combustion temperatures with Applicant's fuel compositions and process, Applicant not only controls or avoids the generation of adverse metallic oxides, but liberates metallics to become principals in a new "clean high energy" class of propellants/fuels and combustion process. Applicant is also able to beneficially apply this discovery of the problem source to non-metallic fuels and systems.

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In essence, Applicant has discovered a combustion process that comprises certain chemical structure/sub-structure and/or mechanical structure/sub-structure that simultaneously 1) increases burning velocity while 2) reducing combustion temperatures, in a vapor phase combustion, whereby a high release rate of what might be known as "free energy" occurs.

In the practice of this invention, methods of incorporating this new class of propellants into existing fuels and systems, e.g. mitigating flash point, vapor pressure, and the like, is disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. **Combustion Temperature Differences**, compares differences in combustion temperatures of differing fuel compositions measured via exhaust gas temperatures at different engine loads.

Figure 2. **Combustion Temperatures and Hydrocarbon Emissions**, compares combustion temperature differences and their relationship to the generation of hydrocarbons emissions.

Figure 3. **Combustion Temperatures and NOx Emissions**, compares combustion temperature differences and their relationship to the generation of NOx emissions.

Figure 4. **Indicated Burning Velocity**, compares the burning velocity of different fuels under differing loads.

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Figure 5. **Burning Velocity and HC Emissions**, compares burning velocity to the generation of HC emissions.

Figure 6. **Burning Velocity and NOx Emissions**, compares burning velocity to the generation of NOx emissions.

Figure 7. **Comparative Distillation Curves** shows distillation ranges for MTBE and DMC containing fuels, achieving object of Applicant's invention.

Figure 8. **Technical Enleanment Due to Distillation Depression** shows warm driveability, emission and combustion improvements of MTBE/oxygen containing gasolines, due to maintaining minimum distillation temperatures for fuel containing oxygenated compounds.

15 DETAILED DESCRIPTION OF INVENTION

Applicant's discovery is discovery of the original source of the heavy metallic oxide problem and its attendant solution, e.g increasing burning velocity and/or reducing combustion temperatures.

20 Accordingly, Applicant discloses herein multiple methods and compositions that increase burning velocity and reduce combustion temperature, which solve this problem. The unity of Applicant's invention is based upon the discovery of the problem's source, and that the solution
25 has many aspects.

In Applicant's improved combustion conditions, the metallic, itself (in preferred but not required practices), becomes an integral and powerful agent in the combustion

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process, itself, and unexpectedly improves combustion thermal efficiencies, fuel economy, net available work, power generation, thrust, and the like; while simultaneously reducing hazardous pollutants.

5 Applicant expects significant combustion and energy conversion improvements at altitude in the case of aviation jet systems, aviation gasoline engines. Similar improvements are contemplated for a wide range of applications, e.g. diesel, gasoline, fuel oils, gas oil
10 turbines, etc.

 In the context of this invention, Applicant generally refers to thermal efficiency, hereinafter, in both its chemical and mechanical context, e.g. the efficiency of the combustion process and amount of useful work generated in
15 the system, e.g. free energy.

 Applicant has found in virtually every case, thermal efficiency, particularly as measured as a function of net useful work generated by the system is increased. Often very substantially. Simultaneously, due to the cool nature
20 of the combustion temperatures, combustion systems will enjoy extended useful life, ease of operation, and improve performance.

 For example, Applicant's has unexpectedly discovered thermal and/or combustion efficiency (e.g. completeness of
25 combustion, etc.) over existing fuels and combustion systems to be on the order of 2.0% to 20%. And, depending upon the circumstances average improvements can range from 2.0% to 5.0%, 5.0% to 10.0% or higher, modest improvements

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range from 0.05% to 1.0% to 2.0%. Exceptional improvements will range from 10%, 25% to 40%, 30% to 80%, or more.

Additionally, Applicant ultimately expects improvements on the order of 5% to 25%, or more, due to modifications of combustion and fuel injection systems designed to optimize the unique combustion features of Applicant's invention.

The invention fundamentally resides in increasing 1) burning velocity of a non-leaded metallic containing fuel by a) increasing laminar burning velocity (by ECS chemical, distillation modification, and/or reformulation means), b) increasing turbulent velocity (by chemical and/or mechanical means) and 2) reducing combustion temperature (by chemical means, e.g. increasing latent heats of vaporization or mechanical means e.g. advanced cooling systems, reducing chamber air charge temperature).

Thus, applicant's invention incorporates multiple interrelating chemical and mechanical elements, all vital to the practice of the invention.

The use of compounds/components and/or chemical and/or mechanical, processes, methods, formulations, reformulations, chemical and non-chemical means, including combinations and sub-combinations thereof, which operate to increase combustion burning velocity and/or reduce combustion temperature (especially simultaneous velocity increases and temperature reductions), are expressly contemplated.

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In the practice of the invention, should an oxygenated compound be employed, maximizing oxygen content is generally desirable. Oxygen contents may range from 0.0001 to 80.0% by weight, or higher, of the composition.

5 Fuel composition, combustion systems, legal concerns dictate. However, beneficial results do not tend to occur until 1.0%, 1.5%, 2.0% or more oxygen is included. More preferred concentrations are 2.0% or more. However, smaller concentrations are acceptable in co-fuel applications. A
10 desirable range is from 0.001 to 30.0% oxygen by weight. Additional weight concentrations of oxygen include 0.001 to 15.0%., 0.5% to 1.5%, 0.3% to 2.7%, 0.4% to 1.8%, 0.5% to 1.9%, 0.6% to 2.0%, 0.7% to 2.1%, 0.8% to 2.2%, 0.9% to 2.3%, 1.0% to 2.4%, 1.1% to 2.5%, 1.2% to 2.6%, 1.8% to
15 2.2%, 2.0% to 3.7%, 0.2% to 0.9%, 1.0% to 4%, 2.0% to 8.0%, 1.8% to 12%, 2.0% to 10.0%, 3.0%, 5.0% to 40%, 2.0% to 53%

 It is anticipated in neat fuel and rocket applications, oxygen concentrations will be significant. In initial co-fuel applications concentrations will be more
20 modest. However, it is an object to include significant concentrations of oxygen which can aggressively react with the metallic, maximizing object of the invention.

 In the practice of this invention, acceptable increases in the rate of the fuel's burning velocity over
25 an unadjusted fuel or combustion system will range from 1.0% to approximately 800%, or more. Velocity increases of 0.2%, 0.5%, 1.0%, 2.0%, 3.5%, 5% to 10.0%, 7.0% to 15.%, 9.0% to 25%, 5.0% to 20%, 12% to 30%, 15% to 40%, 20% to

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50% are desirable. More desirable increases range from 5% to 60%, 10% to 80%, 20% to 100%, 30% to 150%. Other increases are from about 100% to 200%, 100% to 300%. Increases of 200% to 400%, 300% to 600%, 400% to 800%, 500% to 900% are also contemplated and desirable. Increases of 300%, or more, are highly desirable, especially in Applicant's advance fuel and combustion systems. Increases outside these ranges are contemplated and desirable.

New knock sensor technology will be employed in conjunction with higher compression spark ignited engines necessary to practice Applicant's preferred embodiments.

New clean and super clean engine combustion design is contemplated as further embodiment. Improved and new catalytic conversions of exhaust emissions are also contemplated.

Advanced fuel formulation, especially co-fuel formulation or reformulation, which substantially reduces hazardous emissions known or later learned to be hazardous are contemplated. Reformulation optimizing Applicant's preferred embodiments are especially contemplated.

Other advance applications include operation of large and very large engines under moderate to heavy load.

It is contemplated that many applications of the invention will not be fully appreciated until certain thresholds of operation have been achieved.

For example, and as will be set forth in more detail below, the benefits of improved fuel economies are not be fully enjoyed until engine is operated under moderate,

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moderately heavy to heavy load conditions. Thus, new engine design with taking advantage of greater thermal efficiencies under load are contemplated.

5 Furthermore, absent other adjustments, e.g. reductions in MBT spark advance, enhanced air-fuel ratio's, turbocharging, increased compression, the full benefit of Applicant's invention will not be fully enjoyed.

10 In the practice of Applicant's invention, improvements in ignition and spark timing, combustor design, power plant, and the like, which enhances the unique combustion in engines employing Applicant's new class of fuels is an express embodiment.

15 Additionally, close stoichiometric air-fuel ratio adjustment employing, for example computer enhanced electronics, is expressly contemplated.

20 Increases in the pre-ignition or post-ignition partial pressure of the vaporized fraction is particularly effective in influencing improvements in burning velocity. Thus, the character of the pre-ignition/post-ignition vaporized fraction and those features related to the diffusion of heat and active reaction centers in unburned gases, and the like, are determinative and are intended to be optimized as an object of this invention.

25 It is an object of Applicant's invention that the diffusion of pre/post ignition pre-combustion gases operate to increase the momentum/viscosity of the unburned gas to as close as possible to the viscosity of the burned gas, in order to reduce the viscous drag between the burned and the

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unburned gases. It is the elimination of this drag, where monumental increases in burning velocity are achieved.

The rate of flame propagation relative to unburned gas, in practical fuel-air-residual gas mixtures is a fundamental parameter that directly influences the invention's beneficial objects. Thus, maximizing the elementary reactions that take place in the flame and adapting the mass and thermal diffusivity of the various gaseous species comprising the composition of enhanced combustion (see below), to yield increased combustion burning velocity, is an express embodiment of this invention.

COMBUSTION TEMPERATURE MODIFICATION PRACTICE

Reducing combustion temperatures and improving burning velocities are expressly contemplated. One such means is by reducing or eliminating higher boiling point hydrocarbons having lower relative latent heats of vaporization ("LHV"), as compared to the average LHV of the fuel. For example, Applicant has discovered that by reducing or eliminating higher boiling point alkanes from gasoline boiling fuels, work potential is not lost despite the reduction in fuel end point and T-90 temperatures.

Applicant has unexpectedly discovered that fuel economy improvements occur in such circumstances.

Thus, it is an express object to construct or tailor fuel fractions that increase latent heat of vaporization ("LHV") and/or increase the average burning velocity of the

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fuel, when reducing or modifying T-90, T-50, T-10 temperatures.

Thus, it is an embodiment that modification of hydrocarbon co-fuel's, including T-90, T-50, or T-10
5 distillation temperatures and/or substituent components eliminate low burning velocity and low LHV hydrocarbons to the maximum extent possible.

Thus, by reducing boiling temperatures, e.g. end boiling and T-90 temperatures and simultaneously increasing
10 the fuel's average LHV, combustion temperature are reduced.

Wide boiling fuels benefit from end boiling, T-90 boiling and T-50 reductions, which simultaneously increase LHV, including aviation and automotive gasolines, gas oil turbine fuels, fuel oils, diesel fuels, jet aviation fuels,
15 and the like.

In gasoline boiling range fuels Applicant's preferred practice includes elimination of higher boiling point alkanes over aromatic hydrocarbons, over cyclanes, over alkenes of the same boiling temperature. In fuels, whose
20 initial boiling point is in excess of 160°C (e.g. diesel, aviation jet, fuel oils, gas oil turbine fuels, etc.), the preferred practice generally includes elimination of higher boiling temperature alkanes over aromatics over bi-cyclic hydrocarbons of the same boiling temperature.

Thus, it is an embodiment in wide boiling petroleum fractions, e.g. diesel, heavy diesel, gas oil turbine fuels, wide cut jet fuels (Jet B, JP 4), fuel oils, gasolines, etc., to reduce the fuel's distillation boiling
25

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temperatures, especially end point and/or T 90 temperature by 5⁰F to 20⁰F, 10⁰F to 30⁰F, 20⁰F to 50⁰F, 25⁰F to 60⁰F, 40⁰F to 70⁰F, 50⁰F to 80⁰F, 60⁰F to 90⁰F, 70⁰F to 100⁰F, 80⁰F to 120⁰F, 40⁰F to 150⁰F, 75⁰F to 175⁰F, 60⁰F to 200⁰F, 70⁰F to 225⁰F, 80⁰F to 250⁰F, 90⁰F to 275⁰F, 100⁰F to 280⁰F, 110⁰F to 300⁰F, 120⁰F to 320⁰F, 140⁰F to 350⁰F, or more. It is preferred this practice simultaneously increase the fuel's inherent latent heat of vaporization.

It is a specific embodiment of this invention to reduce end point and T-90 boiling temperatures of co-fuels, which may used either in combination with ECS fuels, or as stand alone fuels.

It is an express embodiment of this invention that fuel's, with reduced end point and/or T-90 fractions, having increased LHV's be used in combination with a high energy metallic compound (as set forth below), and optionally with a ECS compound (as set forth below); whereby reductions in the formation of free carbon in primary combustor zones, reductions in hazardous exhaust emissions, including NOx, reductions or control of manganese oxides on exhaust catalyst beds, and the like, occur. In the case of automotive fuels, this T-90 reduction tends to reduce harmful VOC, hydrocarbon and/or NOx emissions.

Quite unexpectedly, Applicant has discovered that when reducing gasoline t-90 temperatures to less than 270⁰F while increasing LHV above the unadjusted fuel, a material combustion advantage occurs in combination with minor

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amounts of Mn. Applicant has discovered that fuel economy and/or mileage unexpectedly improves, even though higher heating value components had been eliminated in the T-90 reduction.

5 Obviously, this effect is sensitive to the fuel and the components that are eliminated and those that remain after T-90 reduction.

10 In the examples set forth below, Applicant intends they be logically connected to Applicant's single invention, namely an advanced form of combustion resulting from reduced combustion temperature and/or increased burning velocity. For example, Applicant's initial disclosure below relates primarily to temperature reduction obtained by intrinsic fuel modification. Later examples
15 amplify beneficial combustion effect by adding additional burning velocity and combustion temperature reductions by extrinsic means.

20 This unity of invention becomes more obvious as one understands the source of the problem has solved. Thus, despite the plethora of fuels, combustion systems and method, they all tie back to a single hub--a single invention.

25 Certain examples may at first blush appear disconnected, but should later become logically connected once the problem source is fully appreciated. Thus, it is Applicant's intent the structure or substructure of his various examples, which may or may individually deal with

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the same fuel, the same aspect of the problem, or even same combustion system, may non-the-less be combined.

However, due to the scope and multiplicity of examples, Applicant has not attempted to combine all such possibilities in this specification, but believes the specification is self evident as to their combination(s).

Example 1

A method of increasing work potential, fuel economy, reducing combustion emissions of a vehicle operating on a conventional or reformulated gasoline, oxygenate optional, comprising: Reducing the boiling temperature of gasoline such that its boiling temperature at T-90 fraction is no greater than 300°F, 295°F, 290°F, 280°F, 270°F, or 260°F, or less, while simultaneously increasing the fuel's LHV to at least 130, 135, 140, 145, 150, 155, 160, 165, 170 btu/lb; optionally admixing MMT into the composition up to 1/64 or 1/32 gr mn/gal; combusting said composition in a gasoline powered vehicle; whereby fuel economy is improved over unadjusted fuel alone, or unadjusted co-fuel with manganese, or co-fuel with T90 absent LHV increase, or manganese containing co-fuel with T90 absent LHV increase (preferred increases are 0.5, 1.0, 1.5, 2.0, 2.5% or more).

Example 1a

A fuel composition comprising a conventional or reformulated gasoline, an optional oxygenate, a T-90 fraction no greater than 290°F, 280°F, 270°F, 260°F, a latent

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heat of vaporization above 130, 135, 140, 145, 150, 155, 160, 165, 170 btu/lb; optionally MMT up to 1/64, 1/32 gram/gal; optionally a burning velocity exceeding 48, 49, 50, 51, 52, 53, 54 cm/sec; said fuel characterized as improving fuel economy (preferably at least 0.5% or more) over unadjusted fuel or adjusted T90 fuel absent minimum LHV.

Example 2

10 The method of example 1, wherein the fuel additionally comprises a charge temperature reducing amount of a combustion chamber deposit control additive.

Example 3

15 The method of example 1, wherein fuel economy is improved over the clear fuel containing same amount of metallic but not having reduced T-90 temperatures and elevated LHV.

Example 4

20 The examples above, wherein latent heat of vaporization and/or burning velocity of the adjusted T-90 fuel is 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0% greater than non adjusted fuel.

25

Example 5

The examples above, wherein fuel T-90 temperature is less than 310°F, more preferably less than 305°F, 300°F,

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295°F, 290°F, 285°F, 280°F, 275°F, 270°F, 265°F, 260°F, 255°F, 250°F, 245°F, or less; and MMT is included in the amount of 1/32 gr. Mn/gal; and optionally a combustion chamber deposit control additive is employed in sufficient amount; whereby charge temperature is reduced; wherein fuel economy is improved over same unadjusted fuel by at least 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, or more, percentage.

Example 6

The composition of example 5, wherein toxic, CO, HC, and/or NOx emissions are also reduced.

Example 7

The example of 5, wherein MMT is contained in a quality of up to 1/32 gram mn per gallon, wherein fuel economy is improved over unadjusted clear fuel.

Example 8

The example of 7, where an oxygenated ECS compound is employed in excess of 0.5% by weight in the fuel, and wherein the gasoline's mid-range temperature is from 170°F, 175°F to approximately 205°F.

Example 9

The example of 8, wherein the composition comprises an ECS compound in a sufficient concentration to increase average burning velocity of composition by an additional

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5.0%, or more, over clear composition as measured by laminar bunsen burner.

Example 10

5 The example of 9, wherein the addition of the ECS compound is sufficient to reduce average combustion temperatures by 25°F, as measured under load of at least 20 indicated horse power (ihp) (using the equivalent of 350 CID engine).

10 Applicant notes this aspect of his invention (e.g. addition of ECS compound with/or without metallic) as applied to gasoline is especially beneficial when T-90 temperatures are equal to or below approximately 300°F, 280°F, 270°F, 260°F, and optionally when T-50 temperatures
15 are in the range of approximately 160°F to 205°F or 170°F to 205, 180°F to 205°F; or alternative 160°F to 190°F or 160°F to 180°F (particularly in later date applications).

 The application of mid-range temperature control is generally applicable to all wide boiling fuels.

20

COMBUSTION TEMPERATURE MODIFICATION

 In the practice of this invention, preferred reductions in combustion temperatures range from 10°F to 500°F. Reductions of 25°F to 50°F, or more, are desireable.
25 Reductions of 100°F, or more, are desireable. Reductions of 5°F to 15°F, 10°F to 25°F, 15°F to 30°F, 20°F to 40°F, 25°F to 45°F, 30°F to 50°F, 35°F to 60°F, 40°F to 55°F, 45°F to 60°F, 50°F to 65°F, 55°F to 75°F, 65°F to 75°F, 70°F to 95°F, 85°F to

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105°F, 100°F to 120°F, 110°F to 140°F, 100°F to 130°F, 110°F to 150°F, 120°F to 160°F, 150°F to 250°F, 250°F to 450°F, 200°F to 500°F, 300°F to 600°F, 200°F to 800°F, 400°F to 1000°F, 300°F to 900°F, 500°F to 2000°F, 600°F to 2500°F, or more, are preferred, especially with simultaneous increases in burning velocity. Reductions outside above ranges are fully expected, especially as the concentration of the Applicant's enhancement combustion compounds (see below) increase as a percent volume of the fuel composition.

10 In the case of gasoline, reduced exhaust temperature translates into increased power and/or reductions of exhaust catalyst inlet temperatures. It is an express embodiment of this invention that exhaust catalyst inlet temperatures be reduced to avoid catalyst plugging. Henc
15 it is an express object to reduce catalyst inlet temperatures to about 1400°F or less, 1350°F, 1300°F, 1250°F, 1200°F, 1150°F, 1100°F, 1050°F, or less, other temperature sufficient to assure acceptable catalyst activity while avoiding the likely hood of manganese oxide plugging.

20 It is also an express embodiment to reduce combustion temperatures by constructing fuel compositions and/or operating engines to avoid or reduce combustion chamber deposits. Increased combustion chamber deposition is attributed to increased charge temperatures. Thus,
25 combustion chamber reducing deposit additives are expressly contemplated.

Thus, combustion temperature control, absent any other aspect of Applicant's invention, is contemplated to reduce

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emissions and/or as a means to control wash coat deposits from low mn concentrations.

Example 11

5 A method of avoiding the plugging or coating of exhaust catalysts or OBD II monitors or monitoring systems with manganese oxides, said method comprising: mixing a high latent heat of vaporization ECS fuel in sufficient quantity with a conventional unleaded or reformulated
10 unleaded gasoline (preferably formulated to increase LHV) containing 1/64, 1/32 gr or more Mn/gal of MMT, wherein said fuel's combustion and exhaust temperatures are sufficiently reduced that inlet exhaust gas temperature of catalyst is less than 1400°f, more preferably less than
15 1350, 1300, 1250, 1200°F.

Example 12

 A method of avoiding the plugging or coating of exhaust catalysts with manganese oxides, said method
20 comprising: modifying T-90 gasoline temperatures to reduce combustion temperature of a low mn containing fuel, wherein said fuel's combustion and exhaust temperatures are sufficiently reduced that inlet exhaust gas temperature of catalyst is less than 1400°f.

25 Applicant has found temperature reductions to be more significant in higher temperature systems.

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CHEMICAL MEANS

Applicant's invention includes the discovery of a class of chemical compounds, which reduce combustion temperature and/or contain certain free radicals, which are released during the combustion process to perform the object of accelerating burning velocity of Applicant's invention.

The molecular or chemical structure yielding high latent heat and/or accelerated burning velocity, etc., to wit, that structure causing the immediate high kinetic diffusion of the unburnt combustion vapor, etc., and/or otherwise acting in the combustion process to increase burning velocity (and exhaust velocity), and/or reduce combustion (and/or exhaust) temperatures is hereinafter referred to as "Enhanced Combustion Structure or ECS."

Those compounds which contain such structure and/or are otherwise capable of performing the object of this invention are referred to as ECS compounds, e.g. those compounds containing ECS and that perform the object of Applicant's invention.

Applicant has discovered that certain molecular features during combustion are responsible for the rapid diffusion of heat and active reaction centers in unburned gases, including the rapid diffusion of unburned gases in front of the flame front, responsible for increased burning velocities.

As a consequence of this discovery, Applicant has identified certain molecular free radicals, but not limited

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to H, H₂, O, O₂, CO, F, F₂, F₃, N, B, Be, BO, B₂, BF, AL
ALO, CH₃, NH₃, CH, C₂H₂, C₂H₅, Li, ONH, NH, NH₂, OCH₃
(methoxy radicals), OCH, OCH₂, and OH (hydroxyl radicals),
believed to be responsible for this result. Additional
5 chemical structure believed capable of achieving similar
result include Cl, OCOO, COOH, C₂H₅OOC, CH₃CO, OCH₂O,
OCHCO, and CONH₂.

It is an embodiment of this invention that said
radicals freely form during the earliest stages of the
10 combustion process (preferably after ignition); with said
radicals being unstable and having a free or unused valency
electron that can chemically bond. It is highly desirable
that they act as chain carriers in the main chain reaction
of combustion, particularly in combination with metallic
15 combustion.

It is additionally preferred that as a consequence of
said radical combustion activity or other means, that
combustion yields dissociated and unstable molecules and
atoms (e.g. OH, CN, CH, NH, etc.) with subsequent
20 reassociation, leading to continuing combustion, increasing
exhaust velocity.

Applicant has found the heat of formation of his
preferred free radicals to be relatively low. Acceptable
heats of formation for said free radicals typically are
25 less than 150, 100, 75, or 50 K cal mole⁻¹. Other heats of
formation include 34 (CH₃), 26 (C₂H₅), 9.3 (OH), 2.0 (CH₃O)
Kcal mole⁻¹. It is contemplated that negative heats of
formation are also acceptable.

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A positive or low negative heat of formation for the ECS compound containing said free radicals is desirable. Acceptable negative ranges for heats of formation for ECS compounds include those less than approximately -200, -180, -160, -150, -145, -130, -120, -100 Kcal/mol, with more preferred being less than -90, -80, -75, -70, -65 Kcal/mol and the most preferred being less than approximately -60, -55, -50, -45, -40, -35, -30, -20, -10 kcal/mol, or positive in value. The closer to a positive or the higher the positive, the more preferred.

ECS compounds, which easily decompose and/or dissociate generating significant free radicals in compression, early and/or regular ignition or combustion, are desirable. It is desirable that dissociation occurs below normal or normal combustion, compression, or at or near ignition temperatures (above if pre-ignition is a concern). It is desirable that dissociation acts to quickly diffuse unburned vapors in front of the flame front, whereby burning velocity is increased.

It also is particularly desirable that said vapor structure and/or the ECS compound, itself, have high latent heats of vaporization (enthalpy of vaporization), particularly those equal to or greater than 28.0 kJ mole^{-1} , at the compounds boiling point. Other enthalpies of vaporization (at the boiling point) are those equal to or greater than 21, 22, 23, 24, 26, 27, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 40, 42, 43, 45, 47, or higher, kJ mole^{-1} . Generally, the higher the better.

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Preferred boiling point temperatures of ECS compounds are those below 350°C, 325°C, 300°C, 275°C, 250°C, 225°C, 200°C, 175°C, 170°C, 160°C, 150°C, 140°C, 130°C, 120°C, 110°C, 105°C, and 100°C. Preferred latent heats of vaporization of ECS compounds at 60°F are those equal to or greater than 75, 100, 110, 120, 130, 135, 140, 145, 150, 155, 160, 165, 170, 180, 190, 200, 210, 220, 230, 240, 250, 270, 290, 300, 325, 350, 375, 400, 425, 450, 475, 500 btu/lb, or more. It is generally preferred that the latent heat of vaporization of the ECS compound be at least the same as, but more preferably 1.0%, 2.0%, 5.0%, 10%, 25%, 50%, 75%, 100%, 150%, 200%, 250%, 300%, or greater, than any unadjusted base or co-fuel to which the compound might be added. Normally, the higher the differences the better. Applicant has discovered, the higher the relative difference in heat of vaporization, the higher, for example, intake charges can be cooled and the greater the improvements in volumetric efficiency.

Another feature of Applicant's ECS compounds is their superior flame propagation velocity features. As a rule, when combusted in air (as a function of their own constitution and as measured in a laminar Bunsen flame), flame velocities should be equal to or greater than 40, 43, 45, 46, 48, 50, 52, 54, 56, 58, 60, 65, 70, 75, 80, 85, 90, 100, 110, 120, 130, 140, 150 cm/sec. Flame velocities of ECS compounds herein may be measured independently or in the presence of a preferred metallic. Flame velocities of

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ECS compounds in the presence of a metallic are generally expected to be greater, than absent said metallic.

Generally, preferred laminar flame propagation velocities should exceed 55 cm/sec. The higher the better.

5 It is preferred that the flame velocity of an any ECS compound as measured in laminar bunsen flame be at least .05% to 1.5%, 1.0% to 3.0%, 2.0% to 4.0%, 3.0% to 6.0%, 5% to 10%, 7% to 20%, 8.0% to 30.0%, 10% to 40%, 15% to 60%, 30% to 200%, 50% to 300%, or more, than unadjusted co-fuel.

10 It is preferred that ECS compounds rapidly decompose at temperatures slightly to moderately higher than ignition temperatures but below combustion temperatures. Decomposition at higher or even lower temperatures is contemplated, including those below ignition temperatures.
15 However, in the case of gasolines pre-ignition should be avoided.

It is preferred that remaining ECS compounds, which are not consumed in combustion, rapidly decompose when emitted in the atmosphere after combustion. Preferred
20 decomposition have half lives less than 20, 15, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 days and more preferred half lives less than 24, 22, 20, 18, 16, 14, 12, 10, 8, 6, 4, 2 hours or less. Most preferred half lives are less than 1.0, 0.5, 0.25 hours or less.

25 It preferred that ECS compounds be thermally stable in normal handling and operating temperatures up to approximately 150°F-300°F, but readily decomposes at approximately temperatures approaching 300°F to 800°F, 300°F

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to 500°F, more preferably at 400°F to 500°F. However, decomposition at temperatures outside of these and/or may occur for example during injection, compression, or prior to ignition, after ignition, and/or combustion.

5 Preferred fuel chain characteristics of Applicant's organic ECS compounds are those containing limited number of carbon atoms in chain with 6, 5, or 4 or fewer atoms preferred. 3 or 2 carbon atoms or a single carbon are more preferred. Generally, the shorter the carbon chain the
10 length the more preferred the ESC compound.

Example 13

A ECS compound comprising: a maximum carbon chain length of 5, 4, 3, 2, or 1 carbon atom(s); a negative heat
15 of formation of -90, -60 kcal/mole, or less, including a positive heat of formation; a melting point of less than 20, 10, 5, 0, -10, -20, -30, -50 °C, or lower; a boiling temperature greater than 25, 30, 40, 42, 43, 44, 60, 80, 90, 100, 110, 120, 140 °C, or greater; a Bunsen burner
20 laminar flame speed in excess of 40, 45, 48, 50, 55, 60, 65 or 70 cm/sec; a latent heat of vaporization exceeding 80, 90, 100, 120, 130, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 230, 235, 240, 250, 300, 380, 400, 450, 500 BTU/lb at 60°F; thermally
25 stable up to 200°F, 250°F, 300°F, 350°F, 400°F, 450°F, 475°F, 500°F, 600°F, whereinafter rapid decomposition into high kinetic energy free radicals occurs, including at least one or more free radicals selected from the group consisting of

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H, H₂, O, O₂, CO, F, F₂, F₃, N, B, Be, BO, B₂, BF, AL ALO, CH₃, NH₃, CH, C₂H₂, C₂H₅, Li, ONH, NH, NH₂, OCH₃, OCH, OCH₂, and OH, and mixture.

5 Example 14

Example 13, wherein the composition is fuel soluble and contains oxygen by weight in excess of 15%, 20%, 25%, 30%, 33%, 40%, 45%, 50%, 52%, 55%, 58%, 60% or more.

10 Non-limiting examples of compounds that Applicant has initially identified that contain ECS structure and that are likely to be effective in accomplishing this object, include: hydrogen, carbon monoxide, methylene di methyl ether (also known as methylal, dimethoxy methane), carbonic acid dimethyl ester (also known as dimethyl carbonate),
15 diethyl carbonate, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), methyl tertiary amyl ether, methanol, ethanol, propanol, tertiary butyl alcohol, dimethyl ether, other C₃ to C₆ lower molecular weight alcohols, diethylene glycol dimethyl ether, diethylene
20 glycol diethyl ether, dimethyl ether diethyl ether, isopropyl ether, diisopropyl ether, nitromethane, nitroethane, nitropropane, nitrous oxide, dinitrous oxide, nitric oxide, ozone, water, gas hydrates (methane hydrate), hydrogen peroxide, hydroperoxides and similar compounds.
25 Applicant believes many other compounds exist that have not yet been identified, which perform ECS function.

Applicant acknowledges there is great variability in performance and characteristics between possible ECS

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compounds, and that in certain neat and/or co-fuel applications, certain ECS compounds may be less satisfactory than others, or altogether unsatisfactory. Several for example, may be very effective in non-regulated aviation, advanced jet applications, diesel applications, but unacceptable for automotive purposes. Other ECS compounds suffer potential health hazards. For example, MTBE has application in many fuels, but is now recognized as a possible carcinogen or allergen, having a long atmospheric half life.

It is further recognized that differing ECS compounds will be employed in different fuel systems, and that liquid fuel soluble ECS compounds are contemplated in generally all fuel state systems. Solid ECS compounds are normally employed in solid fuel systems, but may be incorporated into liquid or gaseous systems by appropriate means.

Obviously, differing ECS compounds in various systems will elicit differing response. For example, it is expected that in alcohols will elicit lower combustion and exhaust temperatures than ethers, due to differences in latent heats of evaporation. It is also expected that lower molecular weight alcohols and carbonates, decompose at an accelerated rate, when compared to ethers.

ECS compounds may be solids, liquids, gases, and mixture, and may be selected from alcohols, amines, amides, oxalates, esters, di-esters, glycols, ethers, aldehydes, ketones, glycols, glycol ethers, peroxides, phenols, carboxylic acids, acetic acids, oxalic acids, boric acids,

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peroxides, hydroperoxides, esters, orthoesters, aldehydic acids, ketonic acids, hydroxyacids, orthoacids, anhydrides, acetates, acetyls, orthoborates, formic acids, nitrates, di-nitrates, carbonates, di-carbonates, nitro-ethers, and
5 the like.

ECS compounds include compounds containing carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, ethoxalyl, glyoxylyl, methoxy, methylenedioxy, glycolyl, and/or hydroxyl components and/or radicals.

10 ECS compounds containing double C=O or C=N bonds are particularly desirable. Non-limiting examples include oxalates, carbonates, acetyl acetones, dimethyl glyoximes, ethylenediamine tetraacetic acids, and the like.

Additional non-limiting examples of likely ECS
15 compounds include ethylene, propylene, tertiary butylcumyl peroxide, butylene, 1,2-butadiene, 1, 3-butadiene, acetylene hydrocarbons including acetylene, allylene, butene-1, pentene-1, hexene-1; substituted hydrazines, including methylhydrazine, symmetrical dimethylhydrazine,
20 unsymmetrical dimethylhydrazine, hydrazine; ethane, propane, butane, diborane, tetraborane, penta borane, hexaborane, decaborane, aluminum borohydride, beryllium borohydride, lithium borohydride, ammonium nitrate, potassium nitrate, nitric acid, ammonium azide, ammonium perchlorate, lithium
25 perchlorate, potassium perchlorate, nitrogen trioxide, nitrogen dioxide, hydrazoic acid, dicyanogen, hydrocyanic acid, monethylaniline, acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, diborane,

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dimethylamine, diethylenetriamine, ethanol, ethylamine, ethylene diamine, ethylene oxide, ethylenediamine, ethyl nitrate, dimethyl sulfide, furfuryl alcohol, heptene, hydrazine, hydrogen, isoethyl nitrate, isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, methyl nitrate, methylamine, methylacetylene, methylvinyl acetylene, monoethylaniline, nitromethane, nitropropane, nitroglycerine, n-octane, propane, propylene oxide, n-propyl nitrate, o-toluidine, triethylamine, trimethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, xylidine, 2,3-xylidine, lithium borohydride, monomethylhydrazine, pentaborane, and the like.

Other candidate ECS compounds include di-tertiary butyl peroxide, alkyl peroxides, alkyl hydroperoxides, acetyl hydroperoxides. Non-limiting examples of peroxides include tertiary butylcumyl peroxide, di(tertiaryamyl) peroxide, tertiary butyl hydroperoxide, di-tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, acetyl tert-butyl hydroperoxide ($(CH_3)_3COOH$), cyclohexyl (acetyl) hydroperoxide, ethyl (acetyl) hydroperoxide (C_2H_5OOH), diacetyl peroxide, diethyl peroxide, dimethyl peroxide, methyl hydroperoxide (CH_3OOH), acetyl benzoyl peroxide, acetyl peroxide, formic acid, tetramethylolethane, n,n-diethyl formic acid, n,n-dimethyl formic acid, formamide, methyl formate, alkyl nitrates (including ethyl-hexyl nitrate and iso-propyl nitrate), 2,5 dimethyl 2,5 di(tertiary butyl peroxy) hexane, $OHC(CH_2)_4CHO$;

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$\text{CH}_3\text{CHOHCHOHCH}_3$; $(\text{CH}_3)_3\text{CCHOHCH}_3$; $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_3$;
 $(\text{CH}_3)_2\text{COOH}$; $(\text{CH}_3)_3\text{COOH}$; CH_3NO_2 ; CH_3CCCOH ; $(\text{CH}_3)_3\text{CCH}_2\text{COH}$;
 $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$; $\text{HOCH}_2\text{CH}_2\text{OH}$; OCH_2CHCHO ; $(\text{CH}_3)_3\text{CCHO}$;
 $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_3$; $\text{C}_5\text{H}_4\text{O}_2$; $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$; $\text{C}_3\text{H}_7\text{COC}_2\text{H}_5$;
5 $\text{C}_5\text{H}_8\text{O}_2$, CH_3COCHO , ethonanoic acid, methyl glycolate,
glyoxylic acid, phenyl glyoxylic acid, diethylene glycol
ethers, methyl formate, isoamyl formate, 1,2-ethanediol,
dimethyl ether 1,2-ethanediol, ethylene nitrite, ethylene
nitrate, ethylene acetate, ethyl ester formic acid, formic
10 acid, glyoxal, glyceric acid, tetraethoxymethane,
triethoxymethane, trimethoxymethane, oxalic acid, oxalic
ester, oxalic acid dimethyl ester, oxalic acid dipropyl
ester; phenols including 2-methoxyphenol, 3-ethoxytoluene;
acetyl acetone, acetic acid anhydrides, ethyl acetate,
15 methyl acetate, methanediol diacetate, amyl acetat ,
acetonyl acetate, ethanoic acid, 2,4-pentadione,
methanesiol diacetate, ethyl acetate, propanic acid,
ethylene oxide, propylene oxide, ammonium nitrate,
dinitrogen tetroxide, and like.

20 Applicant believes that compounds which have or become
strong chelating agents in combustion are also desireable
ECS candidates. Compounds having the following structure,
and which perform ECS function, are desireable: $\text{R}-\text{OO}$, $\text{R}-$
 $\text{OO}-\text{R}$, $\text{R}-\text{COOOCO}-\text{R}$, $\text{R}-\text{COOCOO}-\text{R}$, $\text{R}-\text{CO}-\text{R}$, $\text{R}-\text{COO}-\text{R}$, $\text{H}_3\text{CO}-\text{R}$, CO_2-
25 R , or $\text{R}-\text{CO}-\text{R}$, wherein any R may be void or absent
structure. R may be different, same, or multiples of
itself. R may be $2(\text{R})$, $3(\text{R})$, $4(\text{R})$, and wherein R may be a
hydrogen, carbethoxy, carbomethoxy, caronyldiocy, carboxy,

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carbyl, ethoxalyl, ethoxy, ethylenedioxy, glycolyl, glyoxylyl, hydroxy, methoxy, methyl, ethyl, propyl, butyl, pentyl, methylenedioxy, acetonyl, acetoxy, acetyl, alkyloxy, benzoxy, or benzoyl radical. Applicant's
5 preferred OH combustion enhancement structure is common to his alcohols, most notably methanol.

Applicant also recognizes that certain duplication exists between various classes in this invention. For example, ECS chemistry may contain certain metals, certain
10 metals may contain ECS chemistry and/or be propellant fuels, ect. It is expressly contemplated that such compounds will have multiple utility, and may, for purposes of this disclosure, represent both the metallic and ECS compound, as set forth herein.

15 Applicant expects a small number of ECS compounds will actually be commercially suitable and elicit optimum performance. It is additionally contemplated that certain ECS compounds will be co-ECS compounds (e.g. co-solvents) and be required to assist the usage of one or more ECS
20 compounds. Co-ECS compounds may also be co-solvents. For example, it may necessary to increase flash point temperatures, reduce RVP, or reduce combustion temperatures of certain high velocity ECS compounds by admixing a ECS co-solvent (see below). It is also expected that certain
25 synergies exist between individual(s) or classes of ECS compounds, enhancing their respective capability.

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The practice of this invention also contemplates admixing water and/or co-ECS compound by separate means, including separate fuel injection.

5 It is contemplated that mutual solvents may be employed to dissolve non-soluble and semi-soluble ECS compounds into the intended fuel composition. However, it is preferred that ECS compounds intended for liquid fuel application be fully soluble in such fuels.

10 Example 14a

A fuel soluble ECS compound having a melting point of less than -50°C, -25°C, -5°C, 0°C, 5°C, 10°C, and a boiling point not less than 40°C, 60°C, 75°C, 85°C, or greater.

15 It is also contemplated that certain mechanical structure will be required to either satisfactorily enhance an ECS compound's burning velocity and/or to reduce combustion temperature aspects e.g. enhanced atomization.

Example 15

20 A post-ignition, pre-combustion composition containing a diffusion increasing amount of ECS, whereby combustion burning velocity is increased.

Example 16

25 A pre-ignition vapor composition containing a diffusion increasing amount of ECS, whereby a minimum flame propagation of 60 cm/sec is achieved by a maximum spark energy of 0.2 mJ, preferably 0.15, 0.10 or less mJ.

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Example 17

The vapor composition of examples 15 and 16, wherein the diffusion increasing ECS vapor is derived from the decomposition product of dimethyl carbonate.

5

Example 18

The composition of examples 15 and 16, wherein the composition is a combustion composition.

10

Thus, those elements, ECS compound/components wherein the above enhanced combustion structure exist, in high relative concentrations and/or which become intermediate and/or initial/pre-combustion and/or combustion structure/product, especially in the vapor charge and/or in the vapor of compression and/or combustion, and which causes rapid diffusion of the flame front, and/or rapid diffusion of uncombusted vapors and/or otherwise accelerates and/or improves combustion are most preferred.

15

The higher the relative volume of enhanced combustion structure as a percent of the volume of uncombusted vapor fraction, the better.

20

Thus, it is an embodiment of this invention to employ a sufficient amount of enhanced combustion structure in the vapor fraction to increase the rate of diffusion. It is contemplated that the diffusion means of Applicant invention additionally incorporate separate laminar and/or turbulent burning velocity increasing means.

25

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ECS compounds preferably should be soluble in the fuel composition to which it is added. However, dispersants or other means, including mutual solvents, may be employed. Alternatively, insoluble or partially soluble ECS compounds
5 may be employed in emulsions and/or by other means, including by separate injection, and/or by hybrid means.

It is contemplated in the practice of this invention ECS compounds need not contain ECS structure, if their use or combination otherwise generates or causes to be
10 generated ECS structure in the compression, ignition and/or combustion process. Thus, in the practice of this invention a compound, which enhances the formation of ECS in the combustion process is deemed to be an ECS compound.

Higher octane oxygenated ECS compounds tend to improve
15 ignition quality. ECS compounds with higher latent heats of evaporation, which reduce compression, post ignition (pre-ignition) and/or reduce combustion temperatures, are particularly preferred.

Emulsions or other combination, including those
20 containing ECS, are also desirable, particularly those capable of causing vapor fraction droplets to explode or to explode outside the spray or to otherwise cause quick diffusion of the vapor fraction. Such non-limiting ECS emulsion compounds include water, methanol, hydrogen
25 peroxide, rape seed oil, and the like.

Thus, fuels containing water are contemplated, such as aqueous gasolines, diesels, jet aviation fuels, distillate fuels, and the like.

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Preferred ECS compounds are relatively simple in molecular structure. In the case of liquid fuels, ECS compounds that do not adversely increase the vapor pressure or flash point of the base fuel at ambient or operating temperatures are more preferred. Acceptable blending vapor pressures range from 0.5 to about 50.0 psi. More desirable blending vapor pressures range from 0.5 to 15.0, 0.5 to 12.0, 0.5 to 10.0, 0.5 to 9.0, 0.5 to 8.0, 0.5 to 7.0 psi, or 0.5 to 6.0 psi, or 0.5 to 5.0 psi, or from 0.5 to 3.0, 0.5 to 1.5, 0.5 to 1.0 psi or less. Individual vapor pressure ranges include 5.4, 5.6, 5.7, 5.9, 6.1, 6.3, 6.6, 6.8, 6.9, 7.1, 7.2, 7.5, 7.6, 7.7, 8.1, 8.3 psi.

Vapor pressure and flash point temperatures can be mitigated or controlled via practice set forth below.

It is preferred that ECS compounds employed directly (as opposed to for example separate injection) in liquid co-fuels do not adversely increase the flash point of such base fuels. In liquid fuel applications, ECS compounds having flash points of

-10°F, 5°F, 10°F, 15°F, 20°F, 25°F, 30°F, 40°F, 50°F, 60°F, 70°F, 80°F or greater are acceptable.

In jet aviation and other applications, flash point temperatures above 30°C, 38°C, 40°C, 60°C, 70°C, 80°C, 90°C, 100°C, 105°C, 110°C, 120°C, 130°C or greater, are acceptable.

However, like vapor pressure, an ECS compound's propensity to reduce flash point temperatures may be mitigated or improved by appropriate means (e.g. co-solvents, salts, co-fuel tailoring, ect.), which is contemplated in this

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invention (see Mitigation Practice, below). Thus, the compound's causal increase in burning velocity and/or reduction of combustion temperature must be weighted cost of flash point and vapor pressure improvements attributed to mitigation means.

ECS compounds, which are non-corrosive and/or which do not adversely effect seals or elastomers are preferred. However, corrosion inhibitors are contemplated, if necessary. For an example, a suitable inhibitor is "DC1 11" available from Du Pont. It is contemplated that this inhibitor should be used at the approximate concentrations of 20 to 30 ppm.

Preferred ECS compounds employed in liquid fuels should have low melting points, below 32°F and preferably below -0°F, or more preferably below -40°F or below -50°F, and most preferably below -80°F. Lower temperatures are also preferred. However, temperature reducing additives such as ethylene glycol monomethyl ether may be employed, if necessary. Again, the ECS compound's causal increase in burning velocity and/or reduction of combustion temperature must be weighted against less than desirable melting points.

It is preferred, though not required, that the ECS compound not be toxic, or at least not highly toxic, or associated with adverse toxicity. It is also preferred that the compound be pumpable at low temperatures, have suitable ignition quality, and be thermally stable as a fuel

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additive, although additives to correct poor thermal stability may be employed.

ECS compounds need not contain oxygen. However, ECS compounds containing oxygen are preferred. Those containing
5 at least 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, or 50% or more oxygen by weight are desirable. Oxygen concentrations greater than 25% by weight are preferred. Most preferred are greater than 40% concentrations.

The amount of oxygen introduced into the system of
10 critical import in advanced high velocity applications. It is contemplated that higher velocity, higher oxygen containing ECS compounds, particularly those with high latent heats of vaporization, represent the more preferred compounds in advanced applications.

15 In the case of preferred metallic usage, it is noted the nucleus of Applicant's invention resides in vapor phase combustion, representing the hub to which the many fuel spokes which are attached.

20 Example 19

A method of creating vapor phase combustion, said method comprising: vaporizing or injecting a fuel of an average particle size not exceeding 70, 60, 50, 40, 30, or less, microns under suitable pressure into an air breathing
25 combustion system; said fuel vapor solely comprised of at least one fuel soluble non-leaded metallic whose oxide's heat of formation is negative and exceeds about -200,000, -225,000, -250,000, -275,000, -300,000, -325,000 or -350,000

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gr calories/mole, and at least one ECS compound having latent heat of evaporation exceeding about 150, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, 230, 240, 250 btu/lb, or greater, @ 60°F and a laminar burning velocity exceeding 40, 42, 43, 44, 45, 46, 47, 48, 49, 50, 52, 54, 56, 58, 60 cm/sec; introducing sufficient temperature to the vapor to cause ignition whereinafter unburned vapor decomposes into reactive high kinetic energy free radicals; diffusing said radicals ahead of the flame front containing said metallic; wherein luminous vapor phase burning occurs; and/or whereupon combustion metallic oxide particles are formed in the submicron range.

Example 19a

The composition of 19, additionally containing an oxidant.

Example 20

A composition of matter comprising at least one ECS compound having a latent heat of evaporation exceeding 200 btu/lb @ 60°F and a laminar burning velocity exceeding 48 cm/sec, and a combustion improving amount of at least one fuel soluble high heating value non-leaded metallic whose oxide's heat of formation is negative and exceeds about -200,000 or -350,000 gr calories/mole, said metal or metallic containing compound, is selected from the metals consisting of aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium,

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gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybden, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium, and mixture;

5 said metallic fuel characterized as capable of (vapor phase) combustion at reduced temperature having increas d power generation capacity.

Example 21

10 The composition of Example 20, additionally comprising a substantial majority, majority, substantial minority, or minority of at least one co-fuel; said combination characterized as having latent heat of vaporization and burning velocity greater than co-fuel alone; wher by

15 combustion temperature of combined fuel is reduced at least 5°F, 10°F, 20°F, 30°F, 40°F, 50°F, 60°F, 70°F, 80°F, 90°F, 100°F, 120°F, 140°F, 150°F, 160°F, 175°F, or lower, compared to co-fuel alone.

20 Example 22

The method of 19, wherein at least one oxygenated ECS compound is contained in the fuel vapor, and wherein the unvaporized fuel's latent heat of vaporization exceeds 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, or 38 kJ mol⁻¹

25 at its boiling temperature, not to exceed about 40°C, 60°C, 70°C, 80°C, 90°C, 95°C, 100°C, 105°C, 110°C, 115°C, 120°C, 130°C, 140°C, 150°C.

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Example 23

The method of Example 19, wherein the metallic vapor is derived from a metallic compound having a high heating value exceeding 4,000, 4,500, 5,000, 5,500, 6,000, 6,500, 7,000, 7,500, 8,000, 8,500, 9,000, 9,500, 10,000, 10,500, 11,000, 11,500, 12,000, 12,500, 13,000, 13,500, 14,000, 14,500, 15,000, 15,500, 16,000, 16,500, 17,000 Kcal/kg, selected from the metals group consisting of aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybden, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium, and mixture.

15

Example 24

The method of 21, wherein the pre-combustion vapor is a product derived from dimethyl carbonate and a cyclomatic manganese compound and wherein the ratio of dimethyl carbonate to organo manganese is less than 2,500 parts to one.

20

Example 25

The methods of 19-24, wherein the pre-ignition vapor is exclusively a combination of an ECS compound (preferably DMC) and at least one organo-manganese compound (referrably MMT), whereby the parts ratio of DMC to manganese, ranges from those equal to or less than 100,000:1 to 1:1, 10,000:1

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to 1:1, 5,000:1 to 1:1, 2,500:1 to 1:1, 2,000:1 to 200:1, 3,000:1 to 1,000:1, 2,500:1 to 500:1, 2,000:1 to 50:1; 1,500:1 to 100:1, 1250:1 to 1:1, 1000:1 to 1:1, 750:1 to 50:1, other acceptable ranges of 500:1 to 20:1, 250:1 to 15:1, 200:1 to 3:1, 50:1 to 5:1; 20:1 to 10:1; and 15:1. Individual concentrations include 2,000:1, 1750:1, 1550:1, 1250:1, 1050:1, 900:1, 800:1, 750:1, 650:1, 550:1, 500:1, 450:1, 350:1, 300:1, 250:1, 200:1, 150:1, 125:1, 100:1, 85:1, 75:1, 70:1, 65:1, 60:1, 55:1, 50:1, 45:1, 40:1, 35:1, 30:1, 25:1, 20:1, 15:1, or 10:1. Rato's will vary depending upon application.

In most application's where DMC and MMT (and/or other organo metallic) are employed as neat ECS fuel, it is preferred that the DMC to metal ratio be less than 5,000:1, 4,500:1, 4,000:1, 3,500:1, 3,000:1, 2,500:1, 2,000:1, 1,500:1, 1,000:1, 950:1, 900:1, 850:1, 800:1, 750:1, 700:1, 650:1, 600:1, 550:1, 500:1, 450:1, 400:1, 350:1, 300:1, 250:1, 200:1, 150:1, 100:1, 90:1, 80:1, 75:1, 65:1, 60:1, 55:1, 50:1, 45:1, 40:1, 35:1, 30:1, 25:1, 20:1, or lower.

Co-Fuels

Applicant's co-fuels are generally carbonaceous or hydrogenous or other compound, or hydrocarbonaceous, and/or other compounds based, including mixture, fuels capabl of combustion. It is an express embodiment of this invention that co-fuels may be employed as minority, substantial minority, majority, or substantial majority components of a ECS/co-fuel combination. The ratio of ECS to co-fuel may

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vary from 1000:1, 100:1, 90:1, 75:1, 50:1, 40:1, 30:1, 25:1, 20:1, 15:1, 12:1, 10:1, 8:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:10, 1:15, 1:20, 1:40, 1:50, 1:100.

5 However, it is an express object of this invention to maximize total ESC vapor in the vapor derived from the ECS/co-fuel combination. Thus, it is an object the ESC vapor be a substantial minority or majoritarian component of any ECS/co-fuel combination, such that said ECS vapor,
10 on a mass/volume basis, is a substantial minority or the majoritarian vapor.

 However, in initial application of Applicant's invention it is contemplated the ECS fuel component will represent the minority component, utilizing existing fuels
15 and distribution systems and combustion system.

 It is preferred that Applicant's initial combinations (e.g. ECS fuel + co-fuel) meet all the particularities of ASTM, government and/or industry requirements regarding the co-fuel employed.

20 Thus, it is contemplated that resultant combined fuel may need adjustment or reformulation to meet minimum ASTM and/or government standards. For example, the combined fuel prior to reformulation may not meet heats of combustion requirements due to the lower heats of certain ECS
25 compounds. Thus, additional high calorific material may need to be added. Or, alternatively, the base co-fuel may be tailored so that the addition of ECS fuel does not avoid ASTM or government specifications.

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Applicant's preferred co-fuels are generally those which enjoy high burning velocities, and higher latent heats of evaporatization than convention or current reformulated fuels. Applicant's co-fuels typically enjoy
5 low or extremely low combustion emissions.

For example, it is an express object of this invention that co-fuels be formulated to reduce to the maximum extent possible emissions of NOx, CO, CO2, HC's, toxics, reactive ozone forming precursors, polynuclear aromatics, benzene,
10 butadiene, formaldehyde, acetaldehyde, and/or any cancer causing or environmental harming substance, either now known or identified in the future.

It is also contemplated that Applicant's co-fuel's be formulated to reduce particulate emissions to the greatest
15 extent possible. It is expressly contemplated that such fuels be formulated (or as a result of the addition of ECS fuel and metallic) have particulate emissions of a particle size less than 10.0, 7.5, 6.0, 5.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 microns, or smaller, and/or reduced to the maximum
20 extent possible.

Applicant's co-fuels can contain reduced amounts of aromatics. Aromatic volume concentrations normally will range from or less than 55, 50, 45, 42, 40, 37, 35, 30, 27, 25, 20, 18, 17, 16, 15, 14, 13, 12, 10, 9, 8, 7, 6, 5, 4,
25 3, 1 volume percent, or aromatic free. Ranges less than 40, 35, 30, 27, 25, 23, 20, 19, 18 percent, or less, are more desirable.

Example 26

The method of 19, wherein the pre-combustion vapor additionally comprises a vapor derived from a co-fuel; said co-fuel characterized as being an alternative fuel, hydrogen, petroleum gas, liquefied petroleum gas, LPG-propane, LPG-butane, natural gas, natural gas liquids, methane, ethane, propane, n-butane, propane-butane mixture, fuel methanol, e.g. M 80, M 90, or M 85 fuels, fuel ethanol, biomass fuels, vegetable oil/ester fuels, rap seed methyl ester, soybean fatty acid esters, aqueous carboneous fuels (including aqueous gasolines and diesels, e.g. Gunnerman A-55/D-55), automotive gasolines (meeting ASTM standards) aviation gasoline fuels, including grade 80, grade 100, grade 100ll (meeting ASTM standards), conventional automotive gasolines, reformulated gasolines (meeting U.S. Clean Air Act § 211 (k), California Air Resources Board, Swedish/European EPEFET standards), low vapor pressure gasolines, low sulfur/no-sulfur gasolines, low octane gasolines, Talbert E-gasolines, alkylate or substantially alkylate fuels (including aviation and automotive gasolines), reformat fuels, substantially reformat fuels, isooctane fuels, substantially isooctane fuels, paraffinic fuels, substantially paraffinic fuels (including optionally n-butane, isopentane, toluene, c7-c10 olefins), kerosine, wide range boiling fuels, gas turbine fuels, including No.0-GT, No.1-GT, No.2-GT, No.3-GT, No.4-GT (meeting ASTM standards), aviation jet turbine fuels including JP-4, JP-5, JP-7, JP-8, JP-9, JP-10, TS, Jet A-1,

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Jet A, Jet B (meeting ASTM standards), military aviation
gasolines, missile fuels, solid and liquid rocket fuels,
monopropellant, multipropellant fuels, hypergolic fuels,
gas oil turbine-engine fuels, including grades 0-4,
5 stratified-charged engine fuels, diesel fuels, including
Grade low sulfur No. 1-D, Grade low sulfur No. 2-D, Grade
No. 1-D, Grade No. 2-D, and Grade No 4-D (meeting ASTM
standards), and older grades Type C-B, Type T-T, Type R-R,
Type S-M, reformulated diesel fuels (meeting CARB or
10 Swedish standards), low/no sulfur hydrotreated low/no
aromatic distillate fuels, toluene fuels, substantially
toluene fuels, naptha fuels, substantially naptha fuels,
fuel oils, including Grade 1, Grade 2, Grade 4 (light),
Grade 4, Grade 5 (light), Grade 5 (heavy), Grade 6, heavy
15 diesel fuels for marine or railroad, including those
complying with ISO DIS 8217 and BS MA 100 standards,
various distillate oils, distillate fuels, substantially
distillate fuels, residual type oils, cycle oils, light
cycle oils, light cycle gas oils, heavy cycle oils, heating
20 oils, heavy cycle gas oils, vacuum oils, burner oils,
furnace oils, coal liquids, SRC-II middle distillate coal
fuels, near coal liquids, powdered coal, coal derivatives,
coal, solid fuels, tar sand fuels, shale oil fuels,
hydrazine, ammonia acetylene, and/or any fuel meeting ASTM
25 specifications, EPA certification standards, CARB or
Swedish European standard, or meeting any industry and/or
any government specification or regulation, present and
future, including mixtures thereof; and optionally being

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non-leaded and a low sulfur or no sulfur and/or low or no phosphorus containing fuel.

Example 27

5 The above example, where the combination composition from which the vapor is derived is characterized as meeting all ASTM, government, and industry specifications and standards of said co-fuel, including minimum distillation temperature, flash point, additive, vapor pressure,
10 composition ranges, ingredients, emissions, heats of combustion, and the like as set forth in the specification.

Example 28

15 The method 26, wherein latent heat of vaporization of said co-fuel was increased to an amount greater than 1.5% of the unadjusted co-fuel prior to its combination with the ECS fuel.

Example 29

20 The method 26, wherein pre combustion vapor additionally comprises at least one additive or detergent, selected from additives which control combustion chamber deposits, valve intake deposits, fuel injector deposits, or other additive as set forth in the specification.

25

Example 30

 The above examples, wherein the vapors from combined ECS/co-fuel powers a large engine under moderate to

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moderately high to high load conditions, (e.g. those greater than 14.0, 15.0, 16.0, 17.0, 18.0, 19.0, 20.0, 21.0, 22.0, 23.0, 24.0, 25.0, 26.0, 27.0, 28.0, 29.0, 30.0, or 35.0 ihp, assuming a 350 cubic inch engine displacement ("CID") equivalent, or alternatively load of 0.04, 0.043, 0.0456, 0.0514, 0.054, 0.057, 0.06, 0.063, 0.066, 0.069, 0.71, 0.74, 0.77, 0.8, 0.84, 0.086, 0.10 ihp/cid); whereby fuel economy and/or thermal efficiencies are increased over co-fuel operation alone by 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0% to 20.0%, or more (2.0% to 30.0% preferred).

It is an express embodiment of Applicant's invention to operate combustion systems under load conditions, especially moderate to heavy load. Applicant's invention is well suited for larger engines, under such load conditions.

Example 31

A method of operating an engine, particularly large engines, having displacement equal to or greater than approximately 1.0, 1.5, 2.0, 3.0, 4.0, 4.5, 5.0, 5.7, 6.0, 6.5 (400 cubic inches) 7.0, 8.0, 10.0, 12.0, 14.0, 15.0, 16.0, 17.0, 18.0, 20.0, 21.0, 22.0, 23.0, 24.0, 25.0, 26.0, 27.0, 28.0, 29.0, 30.0, 35.0, 40.0, 50.0, 60.0, 75.0, 100.0, 150.0, 200.0, 250.0, 300.0, 500.0, 1,000.0 cubic liters, and larger displacements; wherein said engine combusts a fuel containing a combustion improving amount of an ECS compound and suitable metallic, and optionally combusting said fuel in combination with a co-fuel;

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operating said engine under moderate to heavy load; whereby combustion temperatures are reduced and/or fuel economy is improved over co-fuel operation alone.

5 Example 32

The method of Example 33a, wherein said engine is a heavy duty diesel (including Volvo TD 163 ES, TD 123 ES, TD 63 ES, D 12 engines), truck, locomotive, marine, heavy industrial, or similar engine.

10

Example 33

The method of 19, 26, wherein said vapor additionally contains at least one vapor from an engine, carburetor and/or induction/injection and/or combustion chamber deposit system cleaning agent or detergent/dispersant (non-limiting examples include commercially available long-chain dibasic acid derivatives (e.g. succinimides such as HiTec 4450), long-chain aliphatic polyamines (e.g. polyisobutenyl polyamine), or long chain Mannich bases, and/or an ashless
15 detergents, including a polyether amine, polyalkenyl amine, alkenyl succinimide, poly ether amine, polyether amide amine, and mixture), and/or an antioxidant, demulsifer, emulsifer corrosion inhibitor, aromatic solvent, scavenger, diluent oil, mutual solvent, metal deactivator, anti-
20 static, dehazer, drag reducing, anti-foam, re-odorant, stabilizer, flow improver, wax crystal modifier, cetane or octane enhancer/improver, combustion improver, lubricity improver additive, and/or mixture.

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Example 34

The method of example 19-27, wherein said vapor is combusted in an engine or combustor selected from group consisting of rocket engine, Brayton cycle engine, gas oil turbine, aviation jet turbine, diesel (direct injection, turbo charge, lean burn, swirl, variable valve timing and lift), marine, locomotive, aviation gas engine, gasoline/automotive engines (non-limiting examples include low emission, ultra low emission, variable-valve timing and lift, direct fuel injection, three-way catalyst systems, lean burn engines), oil burner, residue burner, oil furnace, high performance burners (for example with flame envelopes with heat release rates of 10,000,000 BTU/ft³-hr), gas burner, gas furnace, internal compression engine, spark-ignited internal combustion engine, lean burn, fast burn, external combustion Stirling or Rankine engine, Otto cycle engine, Miller cycle, two stroke, four stroke, or catalyst system.

20 Latent Heat of Vaporization

It is an express object and embodiment of this invention that Applicant's hydrocarbon co-fuels be constructed or formulated such they enjoy the maximum latent heats of vaporization ("LHV") practical, in light of environmental and industry considerations.

It is a further embodiment that Applicant's co-fuels have individual LHV's higher than a normal unadjusted

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conventional or reformulated fuel (base line) at the date of this invention.

Applicant has discovered that threshold improvements will vary greatly depending upon the unadjusted base line fuel composition, type of fuel, and amount of LHV increase.

However, LHV increases of at least 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5, 25.0, 27.5, 30.0 percentage, or more, compared to unadjusted base line fuel (conventional or reformulated), are contemplated and desirable. For purposes of comparing LHV differences, Applicant's base line fuels are ASTM, industry or equivalent fuels on date of this invention.

It is noted, that heavier fuels, e.g. diesel, jet aviation, gas turbine fuels, etc., often have lower average latent heats of evaporation, on a per weight basis, than do the lower molecular weight gasolines. The higher the boiling point temperatures of a fuel, typically the lower the average LHV per unit of weight.

Depending upon the co-fuel, it is desirable that higher boiling components with latent heats of vaporization of less than approximately 40, 50, 60, 70, 80, 90, 100, 110, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180 btu/lb, or alternatively those less than 650, 700, 750, 760, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 880, 900, 905, 910, 915, 920, 925 btu/gal, or alternatively, those components lower than the equivalent average latent heat of vaporization for an unadjusted fuel,

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be reduced or removed from the fuel composition, whereby average latent heat of vaporization for the new formulated fuel is greater than the unadjusted base line fuel.

5 As noted, Applicant has discovered that optimal reformulating of co-fuels not only includes reduced end point and T-90 distillation temperatures and modification to T-50 temperatures, etc., together with fuel substituent modification (e.g. reducing sulfur, aromatics, olefins, etc.), but additionally requires elevating average LHV, by
10 at least 2.0% (5%, 10% more preferred), or more, over the unadjusted base line fuel. Absent simultaneously elevating LHV's, one may not achieve the full benefit of the invention.

Thus, in the practice of this invention reducing T-90
15 and end boiling temperatures additionally requires reducing or eliminating low LHV components while simultaneously increasing high LHV components, such that resultant co-fuel enjoys enhanced LHV. This is a significant departure from the prior art.

20 For example, in hydrocarbons boiling between about 60°C to approximately 120°C-160°C, Applicant has found aromatic hydrocarbons, alkenes, cyclanes, alkanes, in order of their ranking, to be preferred for purposes of achieving elevated LHV's. It is noted that as boiling temperatures raise
25 aromatic LHV's decline. Between approximately 70°C to about 130°C preference between alkenes and cyclanes are about the same. Between 160°C-180°C to approximately 300°C, bi-cyclic

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hydrocarbons, aromatic hydrocarbons, and alkanes, in order of their ranking, are preferred.

Construction of fuels to achieve increased latent heats of vaporization should be tempered by other factors, including known hazardous emission features of certain components, minimum energy, calorific or heating requirements, burning velocity improvement, etc. For example, while benzene and certain xylenes have elevated LHV they are also known to be environmentally harmful. As set forth herein, the reduction of aromatics has certain other environmental advantages. e.g. reduced carbon formation, etc., but also may reduce LHV. Thus, aromatic reduction should be tempered with reducing higher boiling point aromatics and not lower boiling point aromatics.

Thus, depending upon the fuel composition and type of fuel, the tailoring/formulating of co-fuel compositions (e.g. absent ECS compound and/or metallic) to achieve enhanced LHV's should be such that final formulated co-fuel be equal to or greater than approximately 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, or higher, btu/lb (or equivalent), or higher than the unadjusted base line fuel.

Applicant's co-fuels may also have latent heats of vaporization outside this range and be acceptable.

However, in the case of automotive gasolines Applicant has found that latent heats of vaporization equal or in excess of 115, 120, 125, 130, 135, 140, 145, 150, 152, 153,

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155, 160, 165, 170, 175 BTU/lb, or greater, to be desirable. More preferred LHV's are equal to or in excess of 152, 155, 160, 165, 170 BTU/lb.

5 In the case of aviation gasolines latent heats of vaporization equal to or in excess of 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175 BTU/lb, or greater, are acceptable. More desirable are those exceeding 135, 140, 145, 150, 152, 154, 155, 158, 160, 165 BTU/lb, or more.

10 In the case of diesel fuels, latent heats of vaporization equal to or in excess of 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150 BTU/lb, are acceptable. Those in excess of 110, 115, 120, 125, 130 BTU/lb, or more, are desirable.

15 In the case of jet aviation turbine fuels, LHV's should exceed 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165 BTU/lb. Those in excess 85, 90, 95, 100, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165 BTU/lb. are more desirable. Those in excess of 120, 125, 130, 135, 20 140, 145, 150, 155, 160, 165 BTU/lb. are preferred.

Heavy diesel's LHV's should exceed 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 100, 105, 110, 115, 120, 125, 130, or more, BTU/lb. Those in excess of 100, 102, 110 BTU/lb are 25 desirable.

In the construction or reformulation of Applicant's co-fuels and depending upon the individual co-fuel, it is also desirable that the fuel be constructed so that its

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specific heat be equal to or greater than 0.43, 0.44, 0.45, 0.46, 0.47, 0.48, 0.49, 0.50, 0.51, 0.52, 0.53, 0.54 BTU/lb°F, or greater. Those above 0.46 BTU/lb°F are preferred.

5 It is further desireable that the co-fuel be constructed such that its density is maximized. For example, hydrocarbons boiling from about 60°C to about 110°C, cylcanes, alkenes, alkanes, in order of their ranking are preferred. From about 110°C to about 160°C, aromatic
10 hydrocarbons are ranked the highest. From about 160°C to about 280°C, bi-cyclic hydrocarbons are ranked the highest.

 It is expressly contemplated that formulating fuels with elevated latent heats of vaporization be an independent practice of this invention. However, the
15 preferred practice of this invention contemplates use of ECS structure and/or metallics in said new formulated co-fuels (conventional or reformulated).

Example 35

20 A hydrocarbon fuel composition, selected from the group of co-fuels disclosed above, comprising otherwise a conventional or reformulated composition thereof, whereby said fuel is additionally formulated/reformulated such that its latent heat of vaporization is at least 1%, 1.5%, 2%,
25 2.5%, 3%, 4%, 5%, 6%, 7%, 8%, or greater, compared to the unadjusted base fuel, and whereby said fuel is free of ECS structure and/or metallic compound.

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Example 36

The example of 35, whereby the additionally reformulated hydrocarbon fuel composition is a conventional or reformulated gasoline having a latent of heat of vaporization of at least 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5.0%, 6.0%, 6.5%, 7.0%, 7.5%, 8.0%, or more, greater than an unadjusted conventional or reformulated composition at the date of this invention.

10 Example 37

The example of 35, wherein the latent heat of vaporization of the additionally reformulated hydrocarbon composition is greater than original unadjusted base line composition, and wherein said additionally reformulated composition ("LHV Enhanced Co-fuel Composition") is blend d with at least one ECS compound and/or a metallic, whereby the resultant combined composition meets ASTM, government and/or industry standards.

Out side of constructing the fuel to meet minimum industry and government specifications, Applicant's co-fuels should meet be constructed to acheive maximum realizable latent heats of vaporization.

It is also an embodiment of this invention to construct or formulate Applicant's co-fuels to acheive maximum flame velocity. Applicant has found that C2 to C6 acetylene hydrocarbons offer exceptional burning velocities. C4 to C6 olefins and de-olefins are attractive and offer good velocities. C3 cyclo paraffins and benezene

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are also attractive. Less attractive are paraffins, C7 plus aromatic hydrocarbons. Typically, the shorter the carbon chain length, C6, C5, C4, C3 or lower, the higher the burning velocity. In terms of carbon atoms of the same chain length, n-alkynes are preferred over n-alkenes over n-alkanes. Burning velocity of unsaturated hydrocarbons is higher than saturated hydrocarbons of the same chain length. In unsaturated hydrocarbons with one saturated bond, burning velocity is decreased relative to the increase in molecular weight. Naphthenes and aromatic hydrocarbons have similar rates as paraffins.

Example 38

A co-fuel having elevated latent heat of vaporization of at least 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 10%, 12%, or more, compared to unadjusted base fuel (employing fuels as of date of this Application), and a combustion improving ECS compound and/or metallic structure.

The preferred practice of formulating base fuels to increase their latent heats of vaporization is typically by removal of higher boiling material (e.g. with low latent heats of vaporization and/or low burning velocity) until said oxygen/metals free base hydrocarbon composition has an average latent heat of vaporization equal or greater than 780, 800, 820, 830, 840, 850, 860, 870, 880, 890, 900, 905, 910, 915, 920, 925, 930, 940, 950, 970, 990, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350 btu/gal or more. It is

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desireable that it be greater than 860, 880, 900, 910
btu/gal, or more.

Alternatively, the base co-fuel's latent heat of
vaporization should be in excess of 100, 110, 115, 120,
5 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180,
185, 190, 195, 200, 205, 210 BTU/lb, or more.

While there is no upper limit to said base (co-fuel)
composition's latent heat of vaporization, economic costs
and other practical considerations will control.

10 It is contemplated that Applicant's co-fuels will have
low and extremely evaporative emissions and thus low vapor
pressures.

It is also expressly contemplated that co-fuels
contain necessary additives to reduce existing and/or
15 control future combustion chamber, injector, induction
system, and other fuel or combustion related deposits (see
below), which directly interfere or inhibit combustion
and/or cause emission degradation.

It is expressly contemplated that gasoline co-fuels
20 contain elevated octane value $(R+M)/2$ over current
convention fuels and that diesel fuels contain elevated
cetane value over conventional fuels.

It is expressly contemplated that Applicant's co-fuels
be formulated with greatest reductions, and if possible, be
25 free of sulfur, benzene, polynuclear aromatics, and any
substance now known or later learned to be hazardous to the
environment or human health. For example, limitations of di

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and tri aromatics and particulate matter causing and/or ozone forming aromatics are contemplated.

As noted above, Applicant's co-fuels contemplate distillation fractions, which reduce hazardous emissions and/or cancer causing compounds.

It is generally contemplated that Applicant's co-fuels will be free of lead, phosphorous, sulfur, silicon and/or other harmful metallic or non-metallic compound.

10 METALS PRACTICE

The preferred amount of metals contemplated by this invention requires that combustion be improved and/or pollutants reduced. Thus, depending upon fuel composition, combustion system, combustion temperatures and combustion burning velocities, fuel injection factors, carbon, hydrogen, oxygen contents, and the like, metallics and their respective concentrations can vary greatly.

In the practice of Applicant's invention the metallic may itself be employed as a propellant or co-propellant. Thus, the hydrogen content of the metallic and/or metallic containing fuel should be maximized, to the extent possible. Thus, metallic hydrides or other similar compounds are desirable. Hydrogen containing salts are also desirable.

It is an express embodiment of this invention that the combustion of the metallic be by means of vapor phase burning, e.g. wherein combustion does not take place on the

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surface of the metal, or on and/or within a molten layer of oxide covering the metal, typical of metallic combustion.

Applicant's vapor phase burning object is a very unique aspect of Applicant's invention and characterized by high burning rate and the presence of a luminous reaction zone that extends some distance from the metal's surface, where metallic oxide particles are formed in the submicron range. Vapor phase burning is also characterized has being highly expansive combustion, which yield the thermal and other improvements of Applicant's invention.

Example 39

A method of combusting a metallic wherein said method comprises: introducing a sufficient amount of free radicals having enhanced combustion structure into a combustion chamber; igniting and combusting a metal containing compound in presence of said free radicals at temperature below said metal's oxide boiling point (and preferably above said metal or metallic compound's boiling point); combusting said metal at an accelerated burning rate wherein vapor phase burning occurs, evidenced by a brilliant luminous reaction zone extending some distance from the metal's surface; wherein combustion metallic oxide particles are formed in the submicron range and/or remain in the gaseous state.

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Example 40

The method of example 39, wherein the formed metallic oxides travel at high velocity and their particulate size is less than 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 5 0.05 microns, or less.

As a component of Applicant's invention, in order to achieve the above object, while not required, Applicant prefers the metal's oxide boiling point should be greater than the boiling point of the metal. It is also preferred 10 that the metal be introduced into the combustor as a vapor, however solid, atomized, or particulate introduction is acceptable, so long as the objects of this invention are met. In solid fuel applications, it is contemplated the metallic may be introduced as a solid. In hybrid 15 applications, it may be introduced as either a solid or liquid.

While not required, it is preferred that combustion temperatures also be greater than the metal's (or metallic compound's) boiling temperature.

20 It has been found that higher weight oxygen concentrations in fuel compositions, particularly with higher concentrations of enhanced combustion properties, permit higher acceptable metallic concentrations. Higher average ECS and/or co-fuel densities are often associated 25 with higher acceptable metallic concentrations and higher heat release.

Applicant has found that higher Mn concentrations generally translate into higher heat releases. But that is

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not to say there is no upper metallic limit. Fuel and engine combustion thermal dynamics and stoichiometry dictate upper metallic limits.

5 Metallic or manganese concentrations will vary substantially. non-limiting examples include those varying from 0.001 to over 7.50 grams Mn/gal, 0.001 to over 10.00 grams Mn/gal, 0.001 to over 15.00 grams Mn/gal, 0.001 to over 20.0 grams Mn/gal., 0.001 to over 30.00 grams/Mn/gal., 0.001 to over 50.00 grams/Mn/gal.or more. In certain
10 applications, metallic concentrations equal to or great r than 1/64, 1/32, 1/16, 1/4, 3/8, 1/2, 5/8, 3/4, 1, 1.5, 2.0, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 5.0, 7.5, 10, 15, 20, 25, 26, 27, 30, 33, 35, 40. 50, 55, 60.0, 65, 70, 80, and 90 grams may be desirable. In advance and/or rocket and/or
15 propellant applications, metallic/Mn concentrations can be on the order of 100, 150, 200, 225, 250, 300, 400, 200 to 500, 600, 800 to 1000.0 grams/gal, especially in hypergolic conditions. Concentrations above these ranges are also contemplated.

20 However, manganese ranges for more traditional co-fuel applications will generally range from about 0.001 to about 5.00 grams Mn/gal, 0.001 to about 3.00 grams Mn/gal, 0.001 to about 2.00 grams Mn/gal, 0.001 to 1.00 grams Mn/gal, 0.001 to about 0.50 grams Mn/gal, 0.001 to 0.375 grams
25 Mn/gal, 0.001 to about 0.25 grams Mn/gal, 0.001 to 0.125 grams Mn/gal, 0.001 to 0.0625 grams Mn/gal, 0.034 to 0.125 grams Mn/gal of composition.

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Other metallic or manganese concentrations include

1/128, 1/64, 1/32, 1/16, 3/32, 1/8, 5/32, 3/8, 1/4, 1/2,
3/4, 0.8, 0.825125, 1.0, 1.2, 1.3, 1.4, 1.5, 1.6, 1.656,
1.75, 1.875, 1.90, 2.0, 2.25, 2.3, 2.4, 2.45, 2.5, 2.6,
5 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.3125, 3.4, 3.5, 3.6,
3.7, 3.75, 3.8, 3.875, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5,
4.6, 4.7, 4.75, 4.875, 4.9, 5.0, 5.1, 5.2, 5.3, 5.4, 5.5,
5.6, 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.625, 6.5, 6.6, 6.7,
6.8, 6.9, 7.0, 7.1, 7.2, 7.25, 7.3, 7.375, 7.4, 7.5, 7.55,
10 7.6, 7.8, 7.875, 7.9, 8.0, 8.5, 8.75, 8.875, 9.0, 9.1,
9.25, 9.3, 9.375, 9.4, 9.5, 9.6, 9.7, 9.75, 9.8, 9.875,
9.9, 10.0, 10.125, 10.25, 10.375, 10.5, 10.6, 10.75,
10.875, 11.0, 11.1, 11.2, 11.3, 11.4, 11.5, 11.6, 11.7,
11.75, 11.8, 11.875, 11.9, 12.0, 12.2, 12.3, 12.375, 12.4,
15 12.5, 12.7, 12.75, 12.875, 12.9, 13.0, 13.1, 13.2, 13.2,
13.25, 13.3, 13.375, 13.4, 13.5, 13.6, 13.7, 13.75, 13.8,
13.875, 13.9, 14.0, 14.1, 14.2, 14.3, 14.4, 14.5, 14.6,
14.7, 14.8, 14.9, 15.0, 16.0, 17.0, 18.0, 19.0, 20.0, 21.0,
22.0, 23.0, 24.0, 25.0, 26.0, 27.0, 28.0, 29.0, 30.0, 31.0,
20 32.0, 33.0, 34.0, 35.0, 36.0, 37.0, 38.0, 39.0, 40.0, 41.0
grams/gal.

In the case of diesel fuel applications manganese concentrations greater than 1.0% by weight of the fuel or approximately 25 to 33 grams/gal are also contemplated. In
25 gasolines, manganese concentrations greater than 1/64, 1/32, or 1/16 gr/gal are desirable.

Ranges vary depending upon the specific metallic, fuels, fuel weight, regulations, advance applications,

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thermodynamics, and the extent combustion systems are modified to enhance the accelerated low temperature high energy nature of Applicant's invention.

5 Applicant's metals also include a full range of combustion catalysts including ferreous picrate, potassium salts, etc. For example, potassium salts are contemplated including those commercially marketed by Shell Chemical, known as "SparkAid or SparkAde."

10 Such salts may be employed in fuels at 0.01, 0.4, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0, 5.0 parts metallic per million fuel, 1.0 to 4.0 ppm metallic being contemplated, with concentrations less than 16.0 ppm metallic also contemplated. Other potassium salt or ferrocene ranges vary from 0.10 to 8.0, 4.0 to 9.0, 5.0 to 12.0, 6.0 to 13.0, 7.0
15 to 14.0, 8.0 to 15.0 ppm metal per million, 9.0 to 16.0, 10.0 to 20.0, 11.0 to 22.0, 12.0 to 25.0, 13.0 to 30.0, 14.0 to 40.0, 15.0 to 50.0, 16.0 to 60.0, 17.0 to 80.0, 18.0 to 100.0 parts metallic or salt per million fuel.

20 In the application of Applicant's invention potassium concentrations greater than 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, 16.0, 17.0, 18.0, 19.0, 20.0, 21.0, 22.0, 23.0, 24.0, 35.0, 26.0, 27.0, 28.0, 29.0, 30.0 ppm metal (or salt) are expressly contemplated and desireable, and depending upon ECS chemistry and
25 mechanical means employed, said potassium concentrations or greater concentrations can be employed absent adverse metallic oxide formation.

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Metallic concentrations that maximize combustion velocity and/or the other objects of this invention are expressly contemplated.

5 In accordance with this invention, Applicant's fuels will contain that amount of at least one Mn and/or other non-lead metallic, which constitutes a combustion improving amount consistent with the fuel composition, stoichiometry, EC chemisty, combustion system, efficiencies and power desired, as well as legal and/or environmental
10 considerations.

However, it is expressly contemplated that Applicant's fuel may be absent any metallic at all, e.g. be metal free. That is, Applicant's invention, by accelerating burning velocity and/or reducing combustion temperatures by
15 employing chemical and/or mechanical means set forth herein, can be employed absent a metallic. That is, fuels which due to their combustion chemistry, and/or the operating conditions require reductions in hazardous combustion emissions and/or improvements in fuel economy,
20 may employ Applicant's invention absent metallics.

It is an embodiment of this invention to substitute or combine various metallics (e.g. mix them), including substituting or mixing similar and/or different metallics of different compound groups or with the same or similar
25 compound group, or substituting or mixing metals of the same group or subgroup, with each other or any other metallic compound group or metal. Thus, Applicant's invention contemplates substantial variation in metal

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substitution and/or metal mixing, including variation in mix ratios, mix ingredients, metal compounds, etc. See for example U.S. Patents 3,353,938; 3,718,444; 4,139,349.

Thus, it is expressly contemplated that any non-lead metal, or any non-lead organo-metallic, non-lead inorganic metallics, oxygenated organo-metallic or oxygenated inorganic-metallic compounds, and/or any of their related high heat releasing and/or combustion improving metallic compounds, may be employed, mixed in varying proportions, and/or substituted for each other and/or replaced by any non-lead metallic or non-metallic (organic or inorganic) accomplishing the object of this invention.

Example 41

A combustion improving amount of a potassium salt and at least one organo-manganese compound, together with a fuel amount of at least one ECS compound.

It is contemplated that Applicant's metals may be blended with one or more metals or non-metals in varying proportions to achieve synergistic improvements in heat releases, burning velocity (e.g. vapor phase burning), thermal efficiency, emission reductions, power generation, and the like.

Contemplated metallics include all non-lead metals and related compounds whose combustion product has negative high heat of formation. As noted above, contemplated metals and/or metallic compounds should have high heats of combustion or heating values. Preferred negative heats of

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formation, for example of related metallic oxides, should exceed -100,000 to -150,000 gr calories/mole. More preferred are those exceeding -200,000, -225,000, -250,000, -275,000, -300,000, -325,000 -350,000, - 400,000 gr calories/mole., and greater.

It desirable that the elemental metal be of a lower molecular weight, if practical. Acceptable molecular weights of Applicant's metals include those less than 36; more acceptable include those less than 32; desirable molecular weights are those less than 26; more desirable are those less than 15; and even more desirable are those less than 14; with the most desirable being those less than 6.

Non-limiting examples of acceptable metals include aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybdenum, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium. Applicant's metals may be organo-metallics or inorganic compounds.

Transition metals and metals found in 1A, 1B, 2A, 2B, 3B of the periodic table of elements and their cyclomatic compounds, including cyclopentadienyl carbonyls are expressly desirable. Their preparation is set forth in U.S. Patents Nos. 2,818,416, 3,127,351, 2,818,417, 2,839,552 (incorporated by reference). Applicant has found

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that methyl cyclopentadienyl tricarbonyl groups to be effective.

Cyclomatic compounds that include metals found in 4B, 5B, 6B, 7B, group 8 are also contemplated. Cyclomatic
5 compounds containing more than one metals are contemplated.

Metals and their compounds found in 3A of the Periodic Table of Elements, particularly boron and aluminum are expressly contemplated. Metals may be introduced into combustion with the ECS compound, or in a number of other
10 ways, including via soluble compounds, mutual dispersents/solvents, colloidal media, suspension media, separate injection.

Applicant believes that those metallics or metallic compounds, which are generally fuel soluble, having melting
15 and boiling ranges compatible with liquid hydrocarbon combustion present the best immediate option.

Because Applicant's invention also contemplates gaseous and solid ECS compounds and gaseous and solid co-fuels, metals and/or their related compounds that are
20 gaseous and/or solid are also contemplated.

Applicant generally prefers elemental metals of low molecular weight and their compounds, although their heating value and the nature of any co-fuel and combustion system will also dictate choice. It is also preferred the
25 combustion products of element and/or its compounds be environmentally friendly, e.g. low toxicity.

Applicant recognizes that there is a wide number of metallics available in the practice of instant invention.

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Non-limiting examples include cyclopentadienyl methylcyclopentadienyl iron, ferrocene, methylferrocene, and butadiene iron tricarbonyl, butadiene iron tricarbonyl, dicyclopentadienyl iron and dicyclopentadienyl iron compounds (see U.S. Patents 2,680,; 2,804,468; 3,341,311); nickel, cyclopentadienyl nickel nitrosyl; molybdenum hexacarbonyl, cyclopentadienyl molybdenum carbonyls (see U.S. Patent 3,272,606, 3,718,444), compounds of technetium, magnesium, rhenium (see Canadian Patent #1073207.), diborane, tetraborane, hexaborane, and mixture. It is contemplated that organo and non-organic species of these metals will be employed. U.S. Patent # 2,818,416 sets forth many such trimethylaluminum, triethylaluminum, dimethylberyllium, boron hydrate, boron hydride, boron anhydride, triethylboron (C₂H₅)₃B; compounds of boron with hydrogen and lithium, pentaborane, decaborane, barazole, aluminum borohydride, beryllium borohydride, lithium borohydride, and mixtures thereof; light metals compounds (CH₃)₃NBH(CH₃)₃, (CH₃)₂BI, Be(C₂H₅)₂, C₄H₉B(OH)₂, Al(BH₄)₂, Be(BH₄)₂, LiBH₄, B(OC₂H₅)₃, (BO)₃(OCH₃)₃; Zn(CH₃)₂. Compounds with multiple metals are expressly contemplated.

A preferred cyclomatic manganese tricarbonyl is cyclopentadienyl manganese tricarbonyl. A more preferred cyclomatic manganese tricarbonyl is methyl cyclopentadienyl manganese (MMT).

Non-limiting examples of acceptable substitutes include the alkenyl, aralkyl, aralkenyl, cycloalkyl, cycloalkenyl, aryl and alkenyl groups. Illustrative and

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other non-limiting examples of acceptable cyclomatic manganese tricarbonyl antiknock compounds include benzylelopentadienyl manganese tricarbonyl; 1.2-dipropyl 3-cyclohexylcyclopentadienyl manganese tricarbonyl; 1.2-
5 diphenylcyclopentadienyl manganese tricarbonyl; 3-propenylidenyl manganese tricarbonyl; 2-tolylindenyl manganese tricarbonyl; fluorenyl manganese tricarbonyl; 2.3.4.7 - propylfluorenyl manganese tricarbonyl; 3-naphthylfluorenyl manganese tricarbonyl; 4.5.6.7-
10 tetrahydroindenyl manganese tricarbonyl; 3-ethenyl-4, 7-dihydroindenyl manganese tricarbonyl; 2-ethyl 3 (a-phenylethenyl) 4,5,6,7 tetrahydroindenyl manganese tricarbonyl; 3 - (a-cyclohexylidenethenyl) -4.7 -
15 dihydroindenyl manganese tricarbonyl; 1,2,3,4,5,6,7,8 - octahydrofluorenyl manganese tricarbonyl and the like. Mixtures of such compounds can also be used. The above compounds can be generally prepared by methods that are known in the art.

Applicant has found potassium, magnesium, lithium, boron and their related high energy combustible compounds
20 to be particularly effective, and thus desirable. Promoters such as Li and LH are also contemplated, if circumstances require.

All such metal compounds, which advance the object of this invention and/or benefited from the practice of this
25 invention, are a specific embodiment and contemplated in the claims hereto.

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Other non-limiting examples of non-lead metallics have been set forth in the specification. Additional non-limiting examples of non-lead simple binary metallic compounds. Ternary and higher compounds including salts are contemplated. Salts of ternary hydroxy acids are contemplated. Metallic perchlorates, sulfates, nitrates, carbonates, hydroxides, and others, are contemplated. Metal hydroxy compounds are desirable. Contemplated salts also include acid salts containing replaceable hydrogen.

It is also within the scope and practice of this invention to employ oxygenated containing metallic compounds, including oxygenated organo metallic compounds. It is an express embodiment to use metallic compounds, which themselves are ECS compounds. Non-limiting examples would include lithium, iodine, boron based ECS compounds.

Contemplated oxygenated organo metallic compounds include metallic methoxy, dimethoxy, trimethoxy, ethoxy, diethoxy, triethoxy, oxalate, carbonate, dicarbonate, tricarbonate, and similar structure, including mixture thereof. Such oxygenated organo-metallic compounds may be employed with or absent additional ECS compound (e.g. DMC).

Thus, it is in the practice of this invention to employ oxygenate organo metallic compounds, including mixture, as neat fuel, with or absent additional ECS compound, with or absent a co-fuel, with or absent an additional metallic. It is within the practice of this invention to employ a metallic compound, including homologue or analogue having a structure or structure

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similar to $M1-OCH_3$, wherein $M1$ is a metallic having a valence of one or optionally having a valence greater than one, wherein the excess valence is occupied by a double bond oxygen and/or one or more methyl, hydrogen, hydroxy, ethoxy, carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, methylenedioxy radicals, and/or combination thereof; a metallic compound having a structure of $M2-[OCH_3]_2$, wherein $M2$ is a metallic having a valence of two or optionally having a valence greater than two wherein the excess valence are occupied by a double bond oxygen and/or by one or more methyl, hydrogen, hydroxy, ethoxy, carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, methylenedioxy radicals, and/or combination thereof (an illustrative example includes trimethyl borate $[BH(OCH_3)_2]$); a metallic compound having a structure of $M3-[OCH_3]_3$, wherein $M3$ is a metallic having a valence of three or optionally having a valence greater than three wherein the excess valence are occupied by a single or double bond oxygen and/or by one or more methyl, hydrogen, ethoxy, carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, methylenedioxy radical or combination, thereof; a metallic compound having a structure of $M4-[OCH_3]_4$, wherein $M3$ is a metallic having a valence of four or optionally having a valence greater than four wherein the excess valence are occupied by a single or double bond oxygen and/or by one or more methyl, hydrogen, hydroxy, ethoxy, carbethoxy, carbomethoxy, carbonyl,

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carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, methylenedioxy radical or combination, thereof.

In the above examples, it is contemplated M1-M4 may contain one or multiple metals, being either the same or differing metallic. Non-limiting example of said structure containing a multiple same metal includes tetramethoxydiborine [(CH₃O)₄B₂].

Additional contemplated oxygenated-organo metallic structure includes M1-O(CO)O-M2, wherein M1 or M2 are the same or different metals having a valence of 1 or optionally valences greater than one wherein excess valence is occupied by additional metal, and/or M1 or M2 are substituted for a single or double bond oxygen, and/or by one or more methyl, hydrogen, hydroxy, ethoxy, carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, methylenedioxy radical and/or combination thereof. M1 may be substituted for single bond oxygen and/or by one or more methyl, hydrogen, hydroxy, ethoxy, carbethoxy, carbomethoxy, carbonyl, carbonyldioxy, carboxy, methoxy, isonitro, isonitroso, or methylenedioxy radical. Non-limiting examples include lithium carbonate [Li₂O₂(CO)], potassium carbonate [K₂O₂(CO)], sodium carbonate, cesium carbonate, copper carbonate, rubidium carbonate, lithium hydrogen carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, potassium sodium carbonate, and the like.

It is contemplated that C3 and C4 plus ethers may have metallic structure. For example, M'1-CH₂-CH₂-O-CH₂-CH₂-M'2

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structure is contemplated wherein M'1 and M'2 may be same or different metallic or wherein M'1 or M'2 may be hydrogen or atom or radical (similar to those above) with one valence.

5 Other contemplated structure include metallic ketone, ester, alcohol, acid, and the like. Non-limiting examples include M'1-C-OH₃, wherein M'1 is one or more metallic comprising valence of 3; Other structure include M'1-C₂O₄, wherein M'1 has a valence of 2. M₁-C-C-O-C-C-M₂ structure
10 is also contemplated wherein M₁ and M₂ may be same or different metallic or wherein M₂ may be hydrogen or atom of one valence.

 It is highly preferred that said oxygenated organo-metallic compounds have the fuel properties set forth above
15 including those for ECS compounds, e.g. higher heats of vaporization, high burning velocities, decomposition characteristic (e.g. decomposition at post ignition pre-combustion temperatures into enhanced combustion or free radicals structure), be thermally stable at normal handling
20 temperatures, etc.; and have high heat and energy releasing characteristics of metals, etc..

 It is expressly contemplated that Applicant's
 metallics be incorporated into liquid fuel systems by means
 of mutual solvents, as required. Or alternatively, may be
25 introduced into the combustor/combustion chamber by
 seperate means, including liquidification or gasification.

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Applicant's neat oxygenated organo-metallics should be relatively inexpensive to manufacture on a mass production basis.

5 MECHANICAL MEANS

It is contemplated that multiple mechanical means will be employed to enhance burning velocity and/or reduce combustion temperatures of Applicant's ECS based fuels. See Applicant's International Application No. PCT/US95/02691, 10 filed 3/2/95, for detailed description of mechanical means contemplated herein.

The Application of these systems has the beneficial result of improving the combustion, emission, thermal efficiency, fuel economy and other advantages of 15 Applicant's ECS fuels, beyond that which is intrinsic to the ECS fuel alone. Thus, these systems are synergistic, and improvements to ECS fuels go beyond those found for co-fuels alone.

It is anticipated that the mechanical means of 20 Applicant's invention will vary depending upon the fuel and the combustion system contemplated. For example, neat ECS fuel applications, having higher burning velocities, will incorporate differing mechanical means (e.g. higher compression ratio), than co-fuels alone having a lower 25 burning velocity in lower compression ratio combustion systems. Such system are characterized as increasing fuel economy, burning velocity and/or reducing combustion temperature of an ECS based fuel, greater than amount

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attributable to ECS based fuel alone in unmodified system.

Applicant appreciates the mechanical means of this invention, which are synergistic to ECS based fuels, are many. Non-limiting examples include: fuel injection systems, especially those capable of directing a fine uniform atomized spray of vapors at enhanced dynamic flow rates and pressures at desirable angles into combustion chambers (combustors, burners, etc.) advanced evaporators, combustor designs enhancing combustion turbulence, higher combustion chamber inlet pressures (e.g. higher compression ratios), high swirl chambers, swirl combustors, spherical combustors, divided chambers, combustors enhancing combustion efficiency, combustor design enhancing fuel-air mixing, combustion chamber (combustor) design enhancing turbulence and/or fuel-air mixing, engine design maximizing compression (inlet pressure) advantages, engine design maximizing increased power combustion pressure (pressure densities), engine design maximizing lower combustion temperatures, and/or the other advantages of Applicant's invention.

Additional mechanical means, which may be employed and/or adapted, include lean burn systems, catalytic combustors/combustion systems, pre-mixed combustor, diffusion flame combustors, lean premixed pre-evaporizing combustor, pre-evaporizing premixing combustor, variable compression ratio engines, direct injection, direct injection stratified charge engines, three-way catalytic systems, high swirl ratio to lean-air ratio systems

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(particularly during ignition to warm up), variable-valve timing technology (e.g. Honda VTEC technology), turbochargers, port fuel injection systems, tuned intake and exhaust, multiple valves, knock sensors, electronic feedback control, and adaptive learning computer enhanced systems, after-cooling systems, re-entrant combustion chambers, pre-combustion chambers, re-matched inlet port swirl systems, reduced quenching systems, reduced heat transfer systems, enhanced fuel-air mixing systems, enhanced spray atomizer kinetic energy systems, injector designs enhancing fuel-air mixing, water injection systems, computer enhanced systems, combinations thereof, and the like.

In the practice of this invention lean-burn and/or fast burn combustion systems are desirable for purposes of enhancing Applicant's object, particularly with advanced higher oxygen containing fuels.

Mechanical systems employing combustion chambers/combustors, which enhance turbulence are preferred. Non-limiting examples include tumble air motion systems, four valve pent roof combustion chambers, swirl combustion chambers, indirect injection combustion chambers, indirect injection swirl combustion chambers, direct injection combustion chambers, and combustion chambers where geometry, hole diameter, spray angle, compression ratio, and the like, act to enhance turbulence are preferred.

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Injection timing, fuel metering, injection pressures, injection pressure drop, nozzle design, inlet air temperatures, inlet air pressure, droplet size, velocity, pressure and temperature of injected droplets, and combustion chamber geometry are among the influential factors in maximizing the benefits of Applicant's invention, and are incorporated as an express embodiment of this invention.

For example, by varying the nozzle angle, nozzle throat angle, nozzle jet spray centerline eccentricity, spray radius (sphere radius) in a pre-combustion (swirl chamber), and by modifying injection timing, rate, duration, and the like, Applicant can maximize the beneficial attributes of his invention. It is noted, gasoline, diesel fuel, jet turbine, gas oil turbine, fuel oil burner applications are expressly contemplated.

Thus, application, including the injection of highly atomized vapors into the combustion chamber/combustor, and the like, is a particularly desirable object of this invention, especially in turbine, diesel, and fuel oils.

Applicant contemplates a multiplicity of injection and atomization means. Differing fuels, fuel systems, combustion stems require differing injection, atomizing systems, pressures, temperatures, and the like. Obviously, gasoline systems are different than, for example, Grade No. 4-6 fuel oils, which in the practice of this invention, require devices to atomize higher viscosities, and to inject them into burner or combustion chambers at greater

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pressures. The gasoline systems of Applicant invention contemplate injection manifold systems, whereas the diesel systems contemplate direct/indirect injection cylinder systems, etc.

5 With Applicant's high latent heat of vaporization fuels, a vacuum effect can occur when introducing the charge into a cylinder. Consequently, in such conditions varying fuel injection pressures, including low and very low pressures are contemplated.

10 Heavy diesel fuel, fuel oil, and related combustion systems require higher amounts of pressure, load sensing capability, and improved atomization features, when compared to gasoline systems. Jet aviation fuels have similar, yet differing requirements and must, for example,
15 consider fuel flow ranges of 50:1.

For example, in the practice of this invention, contemplated optimum gasoline fuel injection pressures are on the order of 1 to 5, 3 to 15, 5 to 20, 10 to 30, 15 to 45, 20 to 50, 25 to 70 psi.

20 Optimal diesel fuel injection pressures are on the order of 1500 to 30,000 psi. Expected diesel injection pressures in the practice of this invention include 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10,000, 11,000, 12,000 to 18,000, 13,000 to 20,000, 14,000 to 25,000,
25 15,000 to 30,000, 17,000 to 30,000, 18,000 to 30,000, 18,000 to 35,000, 17,000 to 40,000 psi. Lower injection pressures, due to the vacuum effect of Applicant's invention is also expressly contemplated.

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Examples of Applicant's non-limiting atomization systems include: single fluid and multifluid and/or fluid/gas atomizer jets, twin-fluid atomization, internal-mixing atomizers, pressure atomizer, Y-jet atomizers, spinning disk systems, air sprays systems, spray atomizers, vaporizing systems, airblast atomizers, including plain-jet, prefilming, flat air blast atomizer, centrifugal injectors, rotary atomization, rotary wheel injection, ultrasonic, acoustic atomizers and other existing and/or future systems. Air blast atomizers are desirable in the preferred practice of this invention. Applicant's invention anticipates substantial improvements in atomizer technology and incorporates said improvements herein.

Thus, it is a desired and an express embodiment of this invention that the particle (drop size) of injected or vaporized fuels in the combustion chamber be 1 to 70 microns. Preferable average particle sizes are 40 to 60 microns or less, more preferably from 30 to 50 microns, 20 to 40 microns, 5 to 30 microns, or less, including 1 micron or submicron. There is no limitation to the reduction of vapor particle size so long as fuel vapor distribution characteristics are not adversely effected. Average particle sizes greater than 30, 40, 50, or 70 microns are acceptable if rapid diffusion of the vapor fraction occurs by other means, e.g. chemical means, and/or if smaller particle sizes hinder proper fuel distribution characteristic. However, believes that certain applications

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will require a minimum particle size of not greater than 5, 10, 20, 30, 40, 50, or 60 microns.

Cold air induction systems, whereby air intake temperature are reduced are contemplated.

5 In the practice of heavy diesel fuels and companion engines, higher injection pressures with retarded timing under full load conditions yields maximum mixing energy and enhances the burning velocity object of Applicant's invention and is thus preferred.

10 It has been found that lower injection pressures for heavier diesels fuel applications under high speed, but light load conditions, tends to minimize over-mixing and reduces hydrocarbon emissions and is also a preferred practice.

15 Simultaneous fuel injection, by adequate means employing one or more injection systems (e.g. a dual fuel injector), of similar or dissimilar physical state fuels, e.g. gas with a liquid, solid with a liquid, etc., is within the scope of this invention and expressly
20 contemplated. Such application is expressly contemplated where the mixing of an ECS compound with a base co-fuel that may not be possible prior to fuel injection and/or to optimize combustion, which best occurs via separate injection. Separate injection is also contemplated when
25 fuel mixing can not be achieved by other means prior to fuel injection and/or combustion.

For example, the introduction of a liquid hydrocarbon co-fuel and a gaseous ECS fuel, such as hydrogen into a

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combustion chamber or combustor would be accomplished by separate injection, tailored to the specific characteristics of the fuel, and combustion system, designed to maximize combustion burning velocity.

5 Thus, it is contemplated that dissimilar state fuel ingredients may be injected into a combustion system, simultaneously, by singular and/or separate means.

 Various mixing and injection combinations of Applicant's ECS fuels, co-fuels, are contemplated in the
10 context of advanced fuel injection systems and methodology.

 In the case of jet aviation turbine applications, rate tailoring for fuel flow adjustments at altitude is especially preferred, as variations in combustion efficiency occur due to lower ambient pressures.

15 Improved pump line nozzle injection systems, unit injector systems, and/or other systems with high pressure capability, injection rate control, timing control, and/or other sensing controls are especially desirable. Injection systems which can control injection pressure, timing, rate
20 metering, and/or combustion pressures are expressly contemplated.

 In the practice of this invention, direct and indirect fuel injection systems are acceptable. However, direct injection systems are more desirable, especially for
25 diesel applications. Direct fuel injection systems are also more desirable in view of maximizing the higher burning velocities of Applicant's ECS fuels.

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A further embodiment, as noted above, is turbocharging and supercharging, which is highly preferred practice of this invention, especially in gasoline and diesel applications. Advanced air breathing, air pressure apparatus, and/or turbocharge systems, increasing intake air pressures, operate in conjunction ERG systems, are particularly desirable, and substantially enhance the object of this invention.

Advanced cooling, after cooling, and/or coolant systems may also be employed. For example, combustion temperatures can be reduced by reductions in engine coolant temperatures, inlet air temperatures reductions, and/or intake manifold heat inputs. All such means are within the scope of this invention.

Example 42

A method of reducing combustion temperatures and/or increasing burning velocity employing ECS based fuels; said means includes use of at least one system selected from the group consisting advanced evaporators, combustor designs enhancing combustion turbulence, swirl or high swirl combustors or chambers, spherical combustors, divided chambers, enhanced engine design maximizing increased power combustion pressure (pressure densities), engine design maximizing lower combustion temperatures, lean burn systems, catalytic combustors/combustion systems, pre-mixed combustor, diffusion flame combustors, lean premixed pre-evaporizing combustor, pre-evaporizing premixing combustor,

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variable compression ratio engines, indirect injection methods, direct injection methods, direct injection stratified charge engines, three-way catalytic systems, high swirl ratio to lean-air ratio systems (particularly during ignition to warm up), variable-valve timing technology (e.g. Honda VTEC technology), turbo-chargers, port fuel injection systems, tuned intake and exhaust, multiple valves, knock sensors, oxygen sensors, electronic feed-back control, adaptive learning computer enhanced systems, re-entrant combustion chambers, pre-combustion chambers, re-matched inlet port swirl systems, reduced quenching systems, reduced heat transfer systems, enhanced fuel-air mixing systems (including computer enhanced systems), enhanced spray atomizer kinetic energy systems, injector designs enhancing fuel-air mixing, water injection systems, computer enhanced systems, fuel-air adjustment system (including computer enhance systems), lean-burn and/or fast burn combustion systems, tumble air motion systems, four valve pent roof combustion chambers, indirect injection combustors or chambers, indirect injection swirl combustors or chambers, direct injection combustors or chambers, turbulence enhancing combustor or chambers, advanced cooling, after-cooling, coolant systems or air intake systems reducing inlet air temperatures, fuel injection systems (especially those capable of directing a fine uniform atomized spray of vapors at enhanced dynamic flow rates and pressures at desirable angles into combustion chambers, combustors, and burners), and/or other

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mechanical means set forth in the specification; said use characterized as increasing the burning velocity and/or reducing the combustion temperature of an ECS based fuel a amount greater than a co-fuel alone.

5

Example 43

In combination, a combustion improving fuel containing a high latent heat of vaporization oxygenated based ECS compound and a combustion improving amount of a metallic, a combustion system, and an exhaust gas recirculation (ERG) system, wherein said fuel is combusted and exhaust gases are recirculated back into the combustion system; whereby combustion temperature are reduced by at least 10, 20, 30, 40, 50, 100, 150, 200, 250, 300°F, or more.

15

Example 44

The examples of 43, wherein the ERG system is a closed loop system.

20

Example 45

The example of 43, wherein the fuel enjoys an increased burning velocity, and thermal efficiency of the system is improved; whereby fuel economy is increased by at least 0.5%, 1.0%, 2.0%, 5.0%, 10% or more.

25

Applicant's invention also contemplates use of exhaust after treatment systems, with non-limiting examples including ceramic liners, filters, traps, trap-oxidizers, regenerative particulate filters, and exhaust catalysts,

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including three-way catalyst heated by direct electrical power or engine control or other means. The practice of this invention expressly contemplates employing emission control exhaust catalyst, especially in automotive application.

In the practice of this invention it is contemplated, especially in automotive applications to employ an exhaust emissions catalyst (three way catalysts, preferably monolithic catalysts) and to simultaneously employ an on board oxygen sensor, which in part measures the efficiency of the catalyst.

In sum, it is the combination of Applicant's advance combustion improving fuels with applicant's mechanical and related systems, which together, represent significant departure from art.

Thus, it is an embodiment of this invention to vary and/or adapt the above mechanical means to achieve the highest utility of this invention.

20 FUELS AND COMBUSTION SYSTEMS GENERALLY

The combustors contemplated in the practice of this invention include geometric combustors (tubular, annular, turbo-annular, spherical), aerodynamic combustors (diffusion flame, premixing, staged, catalytic, and application combustors (aircraft, industrial, vehicular).

It is preferred in the practice of this invention to employ a diffusion flame combustor, wherein Applicant's combustion flames are further propagated by gaseous jet

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diffusion, advanced droplet evaporation, accelerated burning, and/or spray diffusion.

Thus, it is an embodiment to employ a diffusion flame combustor in combination with ECS fuels; whereby combustion
5 emissions are improved, combustion is accelerated and/or there is a reduction of combustion temperatures.

Applicant's invention is particularly applicable in turbine applications, especially in aviation gas turbines, industrial gas turbines, marine gas turbines, and the like.

10 The physical state of fuels employed in this invention include a wide and narrow boiling range of liquid, semi-liquid, near-liquid, semi-solid, solid, and gaseous fuels, and mixture.

Applicant's neat fuel embodiment (e.g. ECS compound
15 and metallic) has exceptional propulsion and environmental attributes, which are not limiting to internal combustion engines, aviation jet turbines, gas oil turbines, furnaces, burners, air breathing propulsion systems, or rocket engines.

20 Applicant's neat fuel is a stand alone fuel, which may be used potentially in any combustion system. Albeit, modification of existing combustors may be required to accommodate the combustion maximizing and thermal dynamic aspects of such neat applications.

25 It is also an embodiment of this invention to incorporate advanced combustion systems, capable of better converting higher amounts of free energy under higher pressures and/or improved thermal efficiencies resulting

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from the usage of Applicant's fuels. It is anticipated, system modifications and new design will be made to maximize the advantage of the neat, near neat, majority neat, or minority neat ECS fuels of Applicant's invention.

5 Hence, it is an embodiment of this invention to incorporate such advanced combustion systems with Applicant's fuels.

 It is also an express embodiment of Applicant's invention to employ an ECS compound, or mixture, solely by
10 itself, with or without a combustion improving amount of non-lead metallic. However, it is a preferred embodiment to employ an ECS compound, or mixture, together with at least one non-leaded metallic ("ECS Fuel"). It is also an
15 embodiment that Applicant's ECS fuel may contain at least one additional oxidizer and/or at least one addition propellant or a co-fuel.

 In co-fuel practice, e.g. where ECS fuel is combined with hydrogen and/or a carbonaceous fuel, RVP reduction is an express embodiment. However, finished fuels contemplated
20 include those whose RVP ranges from 0.01 psi to 1000.0 psi, 2.0 psi to 200.0 psi, 2.0 psi to 40.0 psi, 1.0 psi to 20.0 psi, 1.0 to 10.0, 1.0 to 8.0 psi, 1.0 psi to 7.5 psi, 1.0 to 7.0 psi, 1.0 to 6.5 psi, 1.0 to 6.0 psi, 1.0 to 3.0 psi, 1.0 to 2.0 psi, or lower.

25 In the case of reformulated gasolines, for example, winter RVP's may range from 11.5 to 12.0 psi and summer RVP's ranging from 6.5 to 6.9 psi.

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It is also an express embodiment to optimize flash point in fuels that specify minimum flash point temperatures, e.g. aviation, turbine and marine applications, etc. It is also anticipated that co-solvent practice, tailoring of hydrocarbon fractions (so as to increase flash point), salts, soaps, and other additives will be employed as required to reduce RVP and/or increase flash point. See Mitigation Practice below.

As noted, reduced concentrations of aromatics are expressly contemplated in Applicant's co-fuels. Reduced concentrations of olefins are also contemplated.

Olefin concentrations of approximately or less than 40, 37, 35, 33, 32, 31, 30, 29, 28, 27, 26, 25, 24, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 volume percentage, or olefin free, are contemplated. Preferred olefins are absent C4 to C5 olefins. In the case of reformulated gasoline an olefin range of 2.0 to 12.0, 3.0 to 10.0, 4.0 to 8.0 volume percent, or less, are contemplated. Olefin free compositions are also contemplated.

Example 46

The method of Example 19, wherein a co-fuel is employed selected from a CARB reformulated diesel fuel, a Swedish/European EPEFET environmental class 1 or 2 diesel fuel, an EPA reformulated diesel fuel, present and future.

Thus, Applicant's invention embodies a neat, essentially neat, majority neat ECS fuel, including

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compositions containing greater than 50% ECS compound(s) by volume. It also embodies a substantial majority, a minority, or substantial minority application, e.g. greater than 0.5%, 1.0%, 1.5%, 1.8%, 2.0%, 2.7%, 3.0%, 3.5%, 3.7%,
5 4.0%, 5%, 10%, 15%, 20%, 25%, 30%, 40% by volume, or weight) of an ECS fuel, normally with a co-fuel ("Base Fuel or Co-Fuel").

In the practice of Applicant's invention, the most preferred neat ECS fuels containing Mn include dimethyl
10 carbonate, methanol, hydrogen, methylal, methane hydrate, hydrazine, and mixtures thereof.

It is initially contemplated Applicant's ECS fuels will likely be incorporated in minority volumes into co-fuels concurrently in the market.

15 However, with greater concentrations of ECS fuels as a volume percent of the finished fuel, combustion and emission properties increase dramatically.

In the more specific co-fuel applications below, Applicant intends that his disclosure of one co-fuel be
20 appropriately applied to any other co-fuel, where application is appropriate (e.g. anti-oxidants or detergents of one co-fuel class can be used with other co-fuel classes, etc.). Likewise, beneficial environmental practice for one fuel may be applied to any other.

25 Co-fuels of Applicant's invention normally will be fuels that are as environmentally attractive as possible, meeting regulatory standards, including California Air

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Resources Board standards, EPA standards, present and future.

Thus co-fuels will generally low in sulfur or be absent sulfur, low or absent carcinogenic polynuclear aromatics, low or absent lead, phosphorus, benzene, toxics, and/or other known or to be discovered carcinogens.

Co-fuels will be formulated (e.g. reformulated) to increase combustion burning velocities and reduce combustion temperature to the maximum extent possible. They will be additionally formulated to achieve maximum environmental advantage. Again practices of one class of fuels (e.g. reformulated gasolines) may be applied in any other class of fuels (e.g. diesel, gas/oil turbine fuels, etc.) to advance the objects of this invention.

15

JET AVIATION TURBINE FUELS AND RELATED TURBINE SYSTEMS

This invention expressly contemplates jet aviation turbine fuel application and co-fuel application. Applicant anticipates wide application in a wide range of jet fuels, aviation turbine engine fuels, including fuels for propulsion and lift engines, starters and auxiliary units.

The practice of this invention expressly embodies aviation turbine, resultant aviation turbine fuels (ECS fuel and co-fuel) or aviation turbine co-fuels, which meet ASTM D 1655 standards, including Jet A, Jet A-1 (a relatively high flash point distillate of the kerosine type), and Jet B-A (a relatively wide boiling range volatile distillate). Other jet turbine grades are

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contemplated, including those meeting IATA guidance manual specifications and military aviation turbine specifications, such as MIL-T-5624, MIL-T-83133, and MIL-P-87107. Thus, Applicant incorporates by reference the
5 numerous specifications of aviation and gas turbine fuel's including ASTM 1655 Specifications and Chapter 2, "Gas Turbine Fuels," L. Gardner and R.B. Whyte, Design of Modern Turbine Combustors, Academic Press, 1990 (pages 81-227).

The aviation turbine fuels of this invention, except as
10 otherwise specified herein, consist of blends of refined hydrocarbons derived from crude petroleum, natural gasoline, or blends thereof with synthetic hydrocarbons. They are generally a mixture of hydrocarbons (i.e. paraffins, cycloparaffins, aromatics, and olefins, plus
15 trace levels of heteroatoms such as sulfur compounds) and blended from straight run distillate fractions, which have been subjected to some form of additional processing.

Aviation turbine fuels, consisting of minor and major portions of ECS material, as disclosed herein are
20 specifically contemplated.

Applicant's invention expressly contemplates gas turbines and air-breathing propulsion systems. Such non-limiting systems include turbojet, turboprop, ducted fan, ram jet, scram jets, ducted jet, pulse jet systems, and
25 their many variations. These systems are contemplated in the instant practice of aviation turbine fuels.

For example, non-limiting gas turbine configurations include basic, one intercooling, two intercooling,

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isothermal intercooling, one reheating, two reheating, isothermal reheating, one intercooling and one reheating, two intercooling and two reheating, isothermal intercooling and isothermal reheating, regeneration, regeneration with basic gas turbine, regeneration with one intercooling, regeneration with one reheating, regeneration with one intercooling and one interheating, regeneration with two intercooling and two reheating, and regeneration with isothermal intercooling and isothermal reheating.

Non-limiting examples of "turbo jet" air breathing propulsion systems include: basic, intercooling, reheating, intercooling and reheating, after-burning, intercooling and reheating. Non-limiting examples of "turbo prop" systems include; basic, intercooling, reheating, intercooling and reheating, regeneration, intercooling and reheating with regeneration, basic ducted fan, intercooling and reheating ducted fan, ducted fan with afterburing, basic ram jet, scream jet, liquid metal cycle nuclear turbo-jet, liquid metal cycle nuclear turbo-prop, ducted rocket and the like.

Applicant has found that ram jet and pulse jet operation represent a particularly preferred embodiment of this invention. Thus, Applicant incorporates by reference the thermal dynamics of the pulse jet. See, "Jet, Rocket, Nuclear, Ion and Electric Propulsion: Theory and Design," Edited and Authored by W.H.T. LOH, 1968, p 191.

The desired combustion chambers of Applicant's turbine combustors include tubular, tubo-annular, annular type, and spherical.

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Applicant's invention has particular application with the above turbine combustion configurations and systems in that it unexpectedly and significantly reduces the formation of free carbon in the primary combustion zone. It has also been found that the reduction of free carbon in the primary combustion zone, in turn reduces flame radiation, which in turn reduces combustion liner temperatures. Thus, reducing liner heat loads and increases engine life.

Furthermore, Applicant's reduced combustion temperatures are extremely useful for high altitude and high mach applications where extreme engine temperatures limit the operation and design of the combustion system. It has been found that Applicant can reduce engine combustion temperatures significantly, on the order of 25°F to 400°F, or more.

Example 47

A method of operating high altitude, high mach or other jet engine exposed to high operating temperature wherein said method comprises: Mixing an ECS fuel (containing an ECS compound and appropriate metallic) in such proportions with an aviation co-fuel that combustion at high mach, exceeding 1.0, 1.5, 2.0, 2.25, 2.5, 2.75, 3.0, 3.25, 3.5, 3.75, 4.0, 4.25, 4.5, 4.75, 5.0, 5.25, 5.5, 5.75, 6.0, 6.25, 6.5 or higher mach, and/or at high or extreme altitude of 30,000, 40,000, 50,000, 60,000, 70,000, 80,000, 90,000, 100,000, 110,000, 120,000, 130,000,

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150,000, 170,000, 200,000, 250,000, 300,000, 350,000 feet above sea level or higher altitudes, is at reduced temperature; operating jet engine at said high mach and/or at high or extreme altitude; wherein engine and combustion temperature is reduced 25°F to 300°F, 50°F to 350°F, 75°F to 375°F, 100°F to 400°F, 125°F to 450°F, 150°F to 500°F, 175°F to 550°F, 200°F to 600°F, 225°F to 750°F, 250°F to 900°F, or more.

It has also been found that Applicant's invention increases useful work, thrust, engine thermal efficiency from 0.5% to 2.0%, 0.5% to 5.0%, 1.0% to 10.0%, 5.0% to 20%, 10% to 40%, 25% to 50%, 35% to 75%, or more, and depending upon character and concentration of the ESC fuel, composition of the co-fuel, and the specific engine operation.

Applicant's invention, in the application of jet turbines, also has particular advantage in reducing hazardous exhaust concentrations of CO, NOx and HC emission's, which are typically associated with idle condition.

As noted above, problematic turbine coating manganese oxides, which have in the past plagued the usage of manganese in turbine fuels are now quite unexpectedly controlled. Applicant's reduction of combustion temperatures also beneficially reduces the coating of other compounds to turbine surfaces and reduces corrosion.

In the practice of this invention, a preferred chemical means employing an ECS compound comprises a

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combustion improving amount of dimethyl carbonate in combination with a combustion improving amount of a cyclomatic manganese tricarbonyl compound in a base aviation jet turbine fuel. It is preferred that the final
5 combination fuel be constructed to meet minimal ASTM specifications, including flash point, pour point, thermal stability, distillation, aromatic, density, freezing point, viscosity, net heat of combustion, and the like.

The hydrocarbon portion of the turbine fuel
10 composition (co-fuel) comprises paraffins, naphthenes, olefins, and aromatics in order of their preference.

It is contemplated that the oxygen derived from ECS compounds fuels will be incorporated into aviation turbine fuels in varying concentrations, with optimal amounts
15 dependent upon average flight altitudes, speed, lift/thrust requirements, combustion system configurations, combustion efficiencies, base fuel hydrocarbon composition, manganese concentrations, and the like.

Assuming an ECS oxygenated means of improving
20 combustion, the recommended O₂ weight percentage concentration of the resultant fuel at sea level to 10,000 feet is from 0.1% to 5.0%, with 3.0% to 5.0% preferred; at 20,000 feet, the recommended O₂ weight percentage 0.1% to 10.0%, with 3.0% to 8.0% being preferred; at 30,000 feet
25 the recommended O₂ weight percentage concentration is from 0.1% to 16.0%, with 5.0% to 7.0% recommended and 5% to 16.0% preferred; at 40,000 feet the recommended O₂ weight percentage concentration is from 0.1% to 30.0%, with 11.0%

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to 30.0% preferred. Recommended average O₂ weight percentage concentration of the resultant fuel may greatly exceed the upper limit of 30.0% or more, particularly in advanced fuel applications, high or extreme high altitudes, with fuel mixes containing alternative oxidants.

Recommended average O₂ weight percentage concentrations of aviation turbine compositions for general distribution, involving co-fuel application, is from about 0.01% to about 50.0%, 1.0% to about 40%, 1.0% to about 20%, 1% to 15%, 1% to 7% oxygen by weight of resultant fuel. 2.0% oxygen by weight is an acceptable concentration. However, 4.5% weight percent is an average preferred concentration. Specific weight percentages of O₂, in co-fuel applications, will vary with any particular fuel, its combustion system, flash point considerations, and operating conditions.

Manganese concentrations will range from 0.001 grams to 10.0 grams per gallon for aviation jet turbine fuel. However, concentrations substantially above this range is anticipated in advanced minority, majority, and/or neat ECS fuel applications. Hypergolic applications also dictate higher concentrations of Mn.

It also appears the higher the altitude of operation, the greater the indicated concentration levels of Mn. Higher concentration levels of manganese are permissible with higher concentrations of oxygen in the composition. As noted, higher concentrations of Oxygen are also indicated at higher altitudes. For example, operating at approximately 40,000 to 50,000 feet above sea level,

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acceptable Mn concentrations can range from about 0.001 to 4.00 grams/gal. At lower altitudes of approximately 5,000 to 20,000 feet above sea level, desireable Mn concentrations range from about 0.001 to 0.50 grams per gallon (those ranging from about 0.125 to 0.50 grams Mn/g being more desireable). However, concentrations outside these ranges are expressly contemplated, especially in more advance operations.

As in the practice of this invention else where, metallic and oxygen concentrations are determined by optimizing the combustion of the composition, in the operating environment of the system.

Example 48

An aviation jet turbine fuel meeting ASTM 1655 specifications, diisopropyl ether or dimethyl carbonate, and mixture, representing 0.5% to 4.5%, 1.0% to 2.0% oxygen weight percent of the composition, and 1/64 to 1/8 g/gal Mn of a cyclopentadienyl manganese tricarbonyl compound.

Example 49

An aviation jet turbine fuel comprising 0.01% to 40.0% by weight oxygen from DMC (more preferably 0.5% to 5.0%, 0.5% to 10.0%) and at least one manganese metallic representing 0.001 to 20.0 gr/gal (more preferably 0.01 to 7.5, 10.0 gr/gal, more preferably 0.1 to 3.0 gr/gal); said fuel having a total aromatic volume concentration not exceeding 25% (22% or less more preferred), a maximum

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sulfur content not exceeding 0.3 weight percent (preferably 0.2, 0.1, 0.02, or lower, or sulfur free), a maximum T-10 temperature of 205°C, a maximum final boiling point temperature of 300°C (more preferably less than 290°C, 285°C, 280°C, 275°C, 270°C, 265°C), a minimum flash point of 38°C, a density of 775 to 840 at 15°C, kg/m³, a minimum freezing point of -40°C, a minimum net heat of combustion of 35.0, 36.0, 37.0, 38.0, 39.0, 40.0, 41.0, 42.0, 42.8, 43.0, 44.0 KJ/kg, a latent heat of vaporization exceeding 90, 95, 100, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175 BTU/lb; whereby combined fuel meets ASTM 1655 finished fuel requirements for either Jet A, Jet A-1, or Jet B;

15 Example 50

A method of employing the fuel of Example 49, in a jet combustor, whereby said method is characterized as increasing the lift and/or operating range of jet employing said fuel, compared to jet aviation co-fuel alone.

20

Example 51

A method employing the fuel of Example 49 above, wherein combustion occurs at an altitude in excess of 10,000 feet above sea level, whereby thermal, combustion efficiency or lift is improved compared to co-fuel alone.

25

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Example 52

A method employing fuel of Example 49, wherein inlet turbine temperature and pressure, and turbine outlet pressure operate jet in excess of mach 3, 4, 5, or 6.

5

Example 53

An aviation jet turbine fuel meeting ASTM 1655 specifications comprising, dimethyl carbonate, a flash point increasing co-solvent, jointly representing 0.5% to 40.0% oxygen weight percent of the composition, and 0.001 to 5.0 g/gal Mn of a cyclopentadienyl manganese tricarbonyl compound.

10

Example 54

Same as examples 49, except that fuel is combusted in an aviation jet engine operating at 5,000 feet altitude above sea level.

15

Example 55

Same as example 49, except the composition is combusted in an aviation jet engine which is operating at 10,000, 20,000 feet altitude above sea level with thermal or combustion efficiency improving at least 1%, 2%, 3%, 4% or more.

20

25

Example 56

Same as example 49, except dimethyl carbonate is in the composition at 25% oxygen weight percent and the

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cyclopentadienyl manganese tricarbonyl compound has a Mn weight in excess of 1.0 gr/gal.

Example 57

5 Same as example 49, except the composition is combusted in an aviation jet engine which is operating at 40,000 feet altitude above sea level.

Example 58

10 The examples of 49, wherein the dimethyl carbonate is in the composition at an oxygen weight of about 0.1 to about 3.0 percent.

Example 58a

15 The examples of 56, 58, wherein the composition contains a flash point increasing amount of tetraethylene glycol, triethylene glycol, co-solvent or salt.

Example 59

20 The examples of 49, wherein said operation is at altitudes in excess of 60,000 feet above sea level, wherein O₂ wt of DMC is 3.0% to 15.0% and metallic is a concentration of 0.5 to 10.0 grams/gal; whereby engine temperatures are by 10°F to 400°F, or more, over known
25 aviation methods.

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Example 60

A method of operating a high altitude jet engine comprising: mixing an aviation jet fuel with an ECS component representing 0.01 to 30.0% oxygen by weight of the composition together with a combustion improving amount of a high energy releasing metallic; operating said engine at altitude in excess of 40,000 feet, preferably 60,000 to 100,000 feet or more; exhausting combustor gases into inlet of a turbine; whereby gas inlet temperature is reduced below 1200°K., 1150°K., 1100°K., 1050°K., 1000°K., 950°K., or at least by 0.5% to 25.0% over best known method for temperature reduction; and/or turbine inlet pressure is increased over existing methods by 0.5% to 40.0%; and/or thermal efficiency is improved by at least 0.5% to 20%, or more, over existing methods.

Example 61

An aviation jet turbine fuel meeting ASTM 1655 specifications containing an oxygenated ECS compound, wherein resultant fuel composition contains 0.5 to 4.0% oxygen weight percent, and at least one cyclopentadienyl manganese tricarbonyl compound at 1/8 gr Mn/gal.

Example 62

In combination, an aviation jet turbine engine and a jet turbine fuel meeting ASTM 1655 specifications containing an oxygenated ECS compound, wherein resultant fuel composition contains 0.5 to 5.0% oxygen weight

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percent, and at least one cyclopentadienyl manganese tricarbonyl compound at 1/8 gr Mn/gal, whereby the formation of free carbon in the primary combustion zone is reduced and inlet temperatures are substantially reduced.

5

Example 63

The combination of example 62, wherein combustion temperatures are reduced, or liner heat loads are reduced and/or turbine engine life is extended.

10

Thus, it is an embodiment of this invention to employ Applicant's advanced ECS based fuel in combination with advance combustors having shorter combustor length to casing diameter ratios than convention combustors; reduced specific fuel consumptions with smaller diameter casting; smaller casing diameters with lower pressure losses, at higher combustion pressures; higher combustion pressure combustors absent increased turbine inlet or liner temperatures; reduced flame tubes sizes that do not sacrifice combustion efficiency, lift, or fuel economy; low pressure lift combustors of reduced flame tubes sizes that do not sacrifice combustion efficiency, lift, or fuel economy; larger diameter combustor casings that enjoy improved lift; larger diameter combustor casings with shorter flame tubes enjoying improved combustion efficiencies; reduced casing diameters absent increasing pressure losses; combustors having reduced pressure losses; lower compression ratio engines; lower compression ratio lift engines; higher compression ratio engines, absent

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adverse flame tube wall temperature increases (hence reducing film air cooling requirements); combustors wherein primary zone combustion efficiency is higher than conventional efficiencies; combustors wherein primary zone is lean or for fuel weak combustion; and the like.

Example 64

In combination, an ECS based aviation jet turbine fuel and a jet engine, the combination characterized by: the combustion of said fuel in a low pressure lift engine, wherein said engine's flame tube length has been decreased by at least 10%, absent impairing lift or combustion efficiency.

Example 65

In combination, an ECS based aviation jet turbine fuel and a jet engine, the combination characterized by: the combustion of said fuel in a high compression engine, wherein said engine's turbine flame tube wall temperatures are reduced and thermal efficiency is increased by at least 5%.

It is an express embodiment of this invention to employ Applicant's combustion improving fuel compositions in combination with traditional or advanced aviation jet turbines combustors, which at high altitudes, including those in excess of 40,000 feet, enjoy improved combustion efficiencies 5% or better, than the co-fuel operating at the same altitude and/or at sea level.

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It is an additional embodiment of this invention to reduce the total distance of the combustor's dilution zone, while simultaneously reducing the outlet stream temperatures. Thus, in the practice of this invention
5 desirable dilution zone length is equal to 1.5 to 2.0 times the flame tube width, especially in engines intended for high altitude cruise. Other desirable dilution zone lengths are equal to 0.9 to 1.5, 1.2 to 1.6, 1.3 to 1.7, 1.4 to 1.6, times the flame tube width.

10 Thus, it is an embodiment of this invention to employ combustors whose dilution zone length is 1.4 to 1.6 times the total flame tube width, while at the same time improving combustion efficiencies at high altitudes. Contemplated combustion efficiencies are greater than 2% at
15 altitudes in excess of 20,000 feet.

In order to prevent local damage to turbine blades, it is a further embodiment of this invention to construct ECS fuel and operate jet combustor such that the outlet stream temperatures (turbine inlet temperatures) be less than
20 1200°K.

Thus it is a further embodiment to operate such systems at turbine inlet temperatures no greater than approximately 1200°K, 1100°K, 1050°K, 1000°K, 950°K, 900°K, 850°K, or less. It is also an embodiment to operate said
25 system at temperatures below 800°K, or less, if practical.

However, to maximize the benefits of Applicant's invention, it is desirable that maximum outlet stream temperatures of the combustor (e.g. maximum turbine entry

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temperatures) not exceed 1100°K. It is also preferred that the average/mean gas temperatures approximate the maximum turbine entry temperature, in order to maintain effective power out put of the engine.

5

Example 66

A method of reducing specific fuel consumption, comprising combusting an ECS fuel and/or an ECS plus co-fuel combination in an annular, tubular or turbo-annular combustor whose dilution zone length is about 1.5 times the flame tube width; whereby specific fuel consumption is reduced.

10

Example 67

The method of example of 66, wherein annular combustor length to casing diameter is reduced with lift and/or fuel efficiency improved.

15

Example 68

The examples of 66, 67, wherein the ECS fuel comprises a majority ASTM aviation jet fuel and a minority comprised of dimethyl carbonate together with a combustion improving amount of at least one non-leaded metallic.

20

Example 71

25

The examples of 66, 67, wherein the combustor operates on a hydrocarbon fuel composition containing a majority fuel component hydrocarbons and a minority comprising of

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dimethyl carbonate and a combustion improving amount of at least one cyclomatic manganese tricarbonyl, wherein outlet stream temperatures are less than 1100°K.

5 Example 72

The examples of 66, 67, wherein the combustor operates on essentially a neat fuel composition comprising dimethyl carbonate and a combustion improving amount of at least one non-leaded metallic or.

10

Example 73

The example of 72, wherein the fuel composition additionally comprises a commercial jet aviation fuel co-fuel.

15

Example 74

The examples of 66, 72, wherein usable work is increased and combustor life is extended by at least 10%.

20 Example 75

The combustor of examples 64, 74, wherein combustion efficiencies at altitudes in excess of 30,000 feet are at least 2% greater than current engines.

25 Example 76

The combustor of examples 74, 75, wherein pressures realized and/or turbine rotational speeds achieved are at least 5% to 20% greater than existing engines.

TABLE 1
Representative Requirements of Aviation Turbine Fuels¹

5	Property		Jet A or Jet A-1	Jet B	ASTM Test Method
	COMPOSITION				
	Acidity, total mg KOH/g	max	0.1	...	D3242
	Aromatics, vol %	max	22 ^c	22 ^c	D1318
10	Sulfur, mercaptan, weight %	max	0.003	0.003	D3227
	Sulfur, total weight %	max	0.3	0.3	D1266 or D1662 or D2622 or D4284
	VOLATILITY				
	Distillation temperature, °C				
15	10% recovered, temp	max	205	...	D86
	20% recovered, temp	max	...	145	
	50% recovered, temp	max	report	190	
	90% recovered, temp	max	report	245	
	Final boiling point, temp	max	300	...	
20	Distillation residue, %	max	1.5	1.6	
	Distillation loss, %	max	1.6	1.5	
	Flash point, °C	min	38	...	D56 or D3828 ^j
	Density at 15°C, kg/m ³		775 to 840	761 to 802	D1298 or D4052
	Vapor pressure, 38°C, kPa	max	...	21	D323
25	FLUIDITY				
	Freezing point, °C	max	-40 Jet A ^E -47 Jet A-1 ^E	-50 ^B	D2388
	Viscosity -20°C, mm ² /s ^L	max	8.0		D445
30	COMBUSTION				
	Net heat of combustion, MJ/kg	min	42.8 ^G	42.8 ^G	D4529, D3338 or D4809
35	One of the following requirements shall be met:				
	(1) Luminometer number, or	min	45	45	D1740
	(2) Smoke point, mm, or	min	25	25	D1322
	(3) Smoke point, mm, and	min	19 ^F	19 ^F	D1322
	Naphthamines, vol, %	max	3	3	D1840
40	CORROSION				
	Copper strip, 2 h at 100°C	max	No. 1	No. 1	D130
45	STABILITY				
	Thermal:				
	Filter pressure drop, mm Hg	max	25 ^K	25 ^K	D3241 ^H
	Tube deposit less than		Code 3	Code 3	
	No Peacock or Abnormal Color Deposits				
50	CONTAMINANTS				
	Existent gum, mg/100 mL	max	7	7	D381
	Water reaction:				
	Interface rating	max	1b	1b	D1094
55	ADDITIVES				
	Electrical conductivity, pS/m		See 5.2	See 5.2	D2524

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The detailed description and practice of preparing Applicant's jet aviation turbine fuels of this invention are set forth in my companion International Application No. PCT/US95/02691, which is incorporated by reference.

5 The fuel specifications of Applicant's jet aviation turbine fuels shall generally comport to requirements of TABLE 1.

As noted, it is desireable to construct Applicant's fuel to reduce combustion temperature as means for
10 increasing LHV. Desired LHV of fuel after adjustment is equal to or above 30, 35, 38, 40, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 68, 70, 72, 74, 76, 78, 80 cal/gram. Preferred LHV's exceed 67, 68, 69, 70 (125 BTU/lb), 71, 72, 73, 74
15 cal/gr.

As noted, it is an embodiment that Applicant's resultant reformulated jet turbine fuel's latent heat of vaporization be higher than those provided by typical ASTM standards.

20 It is an express embodiment to modify Jet A or Jet A-1 fuels to have achieve minimum ASTM freeze and Flash points, if required due to presence of ECS fuel.

The use of aromatics and other means, presented herein, to modify distillation and volatility, while having
25 certain applicability, are generally limited in the case of Jet A and Jet A-1 fuels. But, non-the-less may be applied in warranted circumstances.

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Illustrative example of Applicant's ECS turbine aviation jet fuel combination is as follows:

	Properties	Limits	Limits	Test Method
5	Gravity, deg AFI	37	57	ASTM D287
	Distillation Temp., 10% evaporated	max	400°F (204.4°C)	
	50% evaporated	190.2°C	450°F (232.2°C)	
10	End Point	max	572°F (300°C)	
	Loss, %	max	1.5	
	Residue, %	max	1.5	
15	Sulfur, % by weight	max	0.30	ASTM D1266
	Mercaptan Sulfur, % by weight (See Note 1)	max	0.005	ASTM D1323 or D1219
20	Net Heat of Combustion BTU/lb	18,400	min	ASTM D240
	J/Kg	42.8 x 10 ⁶	min	min
	D2382			
25	Freezing Point, C max	-40 Jet A		
	(See Note 2)	-47 Jet A-1		
	Reid Vapor Pressure, lb m	3		ASTM D323
	Aromatic Content, % by volume	5.0-22	20	ASTM D1319
30	(See Note 3)			
	Burning Quantity			
	Luminometer #	45	min	ASTM D1740
	(See Note 4)			
35	Copper Strip Corrosion, Classification	max	40	ASTM D130
	Temp: 100°C = °			
	212°F = 1.8°			
	Time: 2 hrs.			
40	Viscosity, Cs at -30°F (-34.4°C)	max	15	ASTM D445
	Water Reaction, Volume Change, ml	max	1	ASTM D1094
	Water Reaction, Interface Rating	max	1-b	ASTM D1094
45	ECS Fuel/Compound (O2 wt%, dimethyl carbonate)	0.5-20.0%		0.5-5.0%
50	CMT (g./gal)	1/64-5.0	1/64-2.5	

(continued)

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	Latent Heat of Vaporization (BTU/lb) min	130	125
5	Flash Point, °C min	38	66
10	Laminar burning velocity cm/sec min	48	52
15	Note 1.	Mercaptan sulfur determination may be omitted provided Doctor test per ASTM D484 is conducted and results are negative.	
20	Note 2.	The freezing point shall be at least 6°C below the minimum engine fuel inlet temperature.	
	Note 3.	May contain aromatic up to 25% by volume.	
	Note 4.	Fuels will be acceptable provided they meet one of the following alternative requirements or combination of requirements:	
25	a.	Smoke point of not less than 25 mm when determined per ASTM Method D1322.	
30	b.	Smoke point of not less than 20 mm when determined per ASTM Method D1322 provided fuel does not contain more than 3.0 percent by volume of naphthalene as determined per ASTM D1840.	
35	c.	Due to occasional difficulties meeting the requirement of item b., minimum smoke point may be relaxed down to 18 mm, as necessary, when determined per ASTM method D1322, provided fuel does not contain more than 3.0 percent naphthalene as determined per ASTM D1840.	
40			

Applicant notes, that while aromatic compounds have particular advantage in maintaining fuel stability and/or in modifying fuel volatility, their application in Jet A or Jet A-1 fuels for purposes of modifying temperatures are limited, because T-10 and end-boiling temperatures for said fuels vary only about 100°C. While adverse conditions generally associated with aromatic usage, e.g. free carbon formation, are largely controlled by the practice of this

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invention, such aromatics, otherwise tend to aggravate flame radiation, smoke, and erode elastomers.

Consequently, their usage to the extent possible, should be limited or avoided. However, it is an express embodiment to employ aromatics at concentrations outside those preferred, while still achieving measurable reductions in flame radiation, emissions, etc.

GAS TURBINE FUEL OILS AND SYSTEMS

Applicant's invention expressly contemplates gas turbine fuel oils and co-fuel application of gas turbine fuel oils, and the like, including those meeting suitable requirements of industry, gas oil turbine manufactures, ASTM D 2880 standards, and the like. ASTM fuel specifications D 2880-92, D 396 and D 975 (including future editions), relevant prior specifications, related ASTM standards, test methods, military, and international standards are incorporated by reference. Applicant's companion International Application No. PCT/US95/02691, filed 3/2/95, sets forth Gas Turbine Oils and Systems and is incorporated herein by reference.

A principal object of this invention employing Applicant's solution is the improvement of gas oil turbine thermal efficiency, reduction of harmful deposits, pollution, and control of corrosion on turbine blading.

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Example 77

The method wherein an enhanced combustion vapor is combusted in a gas oil turbine combustor; and is derived from DMC representing 0.01% to 40.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 7.5 gr/gal, and a gas oil turbine co-fuel selected from No. 0-GT, No. 1-GT, No. 2-GT, No. 3-GT or No. 4-GT gas turbine fuel oils; wherein combined fuel is characterized as having a flash point of 38°C to 66°C, a minimum kinetic viscosity at 40°C ranging from 1.3 to 5.5 2mm/s (ASTM D 445), optionally a sulfur content not exceeding 2500, 2000, 1500, 500, 400, 300, 200, 100, 50, 40, 20 ppm wt (or being sulfur free), optionally a T90 temperature reduced at least 20°C compared to unadjusted fuel, a bunsen laminar burning velocity of at least 32, 33, 34, 35, 36, 38, 40, 42, 43, 44 cm/sec, a latent heat of vaporization of at least 80, 85, 90, 95, 100, 105, 110, 115 BTU/lb; whereby turbine inlet gas temperature is less than 650°C, 625°C, 600°C or 550°C., and/or whereby inlet pressure is increased as compared to co-fuel alone (preferably by at least 2.0%, 3.0%, 4.0% or more; optionally harmful deposits, pollution, and corrosion on turbine blading is additionally reduced/controlled; and optionally carbon formation is reduced in the primary combustion zone during combustion of said composition; wherein free carbon formation is also reduced such that inner liner temperatures are reduced with attendant increases in turbine life.

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Example 78

The method of Example 77, wherein said combustor's flame tube has a dilution zone length of approximately 1.4 to 1.6 times the total flame tube width.

5

Example 79

A gas turbine fuel oil composition comprising a 0.01 to 30.0% oxygen by weight DMC and combustion improving amount of a manganese tricarbonyl or other non-leaded fuel soluble metallic compound, and a majority portion of a gas oil turbine fuel, whereby resultant composition meets applicable ASTM D 2880, D 396, and D 975 standards, present and future.

10

15 Example 80

The example of 77, wherein the cyclomatic manganese compound is present in the composition in an amount from about 0.0625 to 3.00 gram Mn/gal, with 0.25 to 1.50 g Mn/gal preferred, with 0.125 to 0.375 g Mn/gal also preferred; and wherein the oxygen content of the resultant fuel does not exceed 4.5% oxygen weight percent.

20

Example 81

The composition of example 62, wherein said composition's end boiling point, T 90, and T-50 temperatures are reduced at least 10°F or 50°F and latent heat of vaporization is increased, whereby combustion temperatures are reduced.

25

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In the practice of this invention, different gas turbine fuels prepared to different specifications and sold under different names are acceptable. However, those that meet the requirements of fuels specified under ASTM Specification D 2880, are preferred.

Desireable gas turbine co-fuels of this invention are homogeneous mixtures of hydrocarbon oils, free of inorganic acid, and free of excessive amounts of solid or fibrous foreign matter, which would otherwise make frequent cleaning of suitable strainers necessary. It is preferred that all grades of turbine fuel oil remain homogeneous in normal storage and not separate by gravity into light and heavy oil components outside the viscosity limits for the grade.

Applicant's turbine fuel oils should be primarily hydrocarbons, but may include bio material and/or coal derivatives. It is also preferred that Applicant's co-fuel turbine fuel oils be free of contaminants. In the present context, contaminants are considered to be foreign materials that make the fuel less suitable or even unsuitable for the intended use. For preferred preparation of turbine co-fuels, see International Application No. PCT/US95/02691.

The various grades of gas turbine fuel oil contemplated in Applicant's invention shall conform to the limiting requirements shown in Table 2. The requirement for Grade No., 1-GT and 2-GT conform in most respects to the corresponding Grade Nos. 1 and 2 fuels of ASTM

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Specification D 396, and to Grade Nos. 1-D and 2-D in ASTM Specification D 975.

The viscosity range of Grade Nos. 3-GT and 4-GT fuel brackets the Grade Nos. 4, 5, and 6 of ASTM Specification D 396 and Grade No. 4-D of ASTM Specification D 975. It is the intent of this invention that fuels meeting ASTM Specification D 396 and D 975 requirements may be employed. Non-limiting examples of acceptable fuels include fuels meeting the requirements of Table 2.

Diesel Fuel Oils and Systems

As noted, this invention contemplates a wide range of diesel fuel oils and related system applications. Non-limiting examples of diesel co-fuels and resultant fuels, include, synthetic diesel, bio diesel (bio esters, soybean, e.g. C18 + fatty acid methyl esters, rap seed, see IFP EsterFip process), etc., fuels meeting ASTM D 975 standards (incorporated by reference), industry, international specifications, including CARB, EPA, European EPEFP specifications, certification standards and/or regulations, present and future. See TABLE 3.

TABLE 2
DETAILED REQUIREMENTS FOR GAS TURBINE FUEL OILS AT TIME AND PLACE
OF CUSTODY TRANSFER TO USER^{A,B}

5	Property	ASTM Test Method ^C	Grade ^D				
			No. O-GT ^E	No. 1-GT	No. 2-GT	No. 3-GT	No. 4-GT
	FLASH POINT	D 93		38 (100)	38 (100)	55 (130)	66 (150)
	°C (°F) min						
10	WATER AND SEDIMENT	D 1798	0.05	0.05	0.05	1.0	1.0
	% vol max						
	DISTILLATION						
	TEMPERATURE	D 86					
15	°C (°F)						
	90% VOL. RECOVERED						
	min		282
	max		...	288	338
	KINEMATIC VISCOSITY						
20	2 mm/g ^F	D 445					
	AT 40 °C (104 °F) min		^G	1.3	1.9	5.5	5.5
	max			2.4	4.1
	AT 100 °C (212 °F) max			50.0	50.0
	RAMSBOTTOM						
25	CARBON RESIDUE	D 524	0.15	0.16	0.35
	on						
	10% DISTILLATION						
	RESIDUE						
	% mass, max						
30	ASH						
	% MASS, max	D 482	0.01	0.01	0.01	0.03	...
	DENSITY at						
	15 °C kg/m ³						
	max		...	850	876
35	POUR POINT ^F	D 97	...	-18	-6
	°C (°F) max						

^A To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

40 ^B Gas turbines with waste heat recovery equipment may require fuel sulfur limits to prevent cold and corrosion. Environmental limits may also apply to fuel sulfur in selected areas in the United States and in other countries.

^C The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 6.1.

45 ^D No. O-GT includes naphtha, Jet B fuel and other volatile hydrocarbon liquids. No. 1-GT corresponds in general to specification D 396 Grade No. 1 fuel and D 975 Grade 1-D diesel fuel in physical properties. No. 2-GT corresponds in general to specification D 396 No. 2 fuel and D 975 Grade 2-D diesel fuel in physical properties. No. 3-GT and No. 4-GT viscosity range brackets specification D 396 Grades No. 4, No. 5 (light), No. 5 (heavy), and No. 6, and D 975 Grade No. 4-D diesel fuel in physical properties.

50 ^E When the flash point is below 38 °C (100 °F) or when kinematic viscosity is below 1.3 mm³/s at 40 °C (104 °F) or when both conditions exist, the turbine manufacturer should be consulted with respect to safe handling and fuel system design.

55 ^F For cold weather operation, the pour point should be specified 6 °C below the ambient temperature at which the turbine is to be operated except where fuel heating facilities are provided. When a pour point less than -18 °C is specified for Grade No. 2-GT, the minimum viscosity shall be 1.7 mm³/s and the minimum 90% recovered temperature shall be waived.

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Example 82

A bio diesel fuel composition comprising: 1.0% to 50% by volume biodiesel (bio-esters, C18 + fatty acid methyl esters, rape seed esters, and the like), 1.0% to 95% by volume diesel fuel oil (conventional or reformulated), optionally 0.5% to 90% alkylate, 1.0% to 90.0% by volume at least one ECS compound, and optionally a combustion improving amount of a metallic; under the proviso that total volume of biodiesel, diesel fuel oil, alkylate, and ECS compound be equal to 100% of the composition's volume (less metallic concentration, if any).

Applicant's diesel fuels include Swedish Enviromental class 1 and 2 fuels, CARB reformulated fuels, and EPA reformulated fuels, existing and future.

Non-limiting examples of diesel fuel engines contemplated in Applicant's invention include: indirect injection, improved indirect injection and advanced ignition assisted diesel engine systems, direct injection, turbo-charge direct injection, existing and future advance swirl chamber engines, existing and future.

Applicant's invention also contemplates exhaust gas treatment via catalyst, trap, and/or other system.

It is an express embodiment of this invention that Applicant's fuels include future reformulated diesel fuels of the calibre to be defined either by industry or government. A preferred embodiment are low/no sulfur, low/no aromatic hydrotreated diesel fuels, absent normally

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associated lubricity problems facing similar or low sulphur fuels.

It is also an express embodiment to include lubricity additives in low/no sulfur fuels.

5

Example 83

A fuel composition comprising at least one ECS compound and a combustion improving amount of at least one metallic; a low/no sulfur and/or low/no aromatic reformulated diesel composition; and a lubricity additive; wherein the gum concentration is approximately 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 mg/100ml.

10

Example 84

The fuel composition of Example 83, additionally comprises combustion chamber, induction valve, or injector deposit control additive, or additive package.

15

Example 85

The fuel composition of Example 83, wherein the diesel fuel has a sulfur content of 0.05 wt% or less, a color standard of less than 2, 1 under ASTM 1500, an aromatic concentration of 25%, 20%, 15%, 10%, or less, a gum concentration of 1.5 to 2.0, or less, mg/100ml.

20

TABLE 3
ASTM D 975
DETAILED REQUIREMENTS FOR DIESEL FUEL OILS⁴

Property	ASTM Test Method ^b	Grade Low Sulfur No. 1-D	Grade Low Sulfur No. 2-D	Grade No. 1-D ^c	Grade No. 2-D ^c	Grade No. 4-D ^c
Flash Point, °C, min.	D93	38	52	38	52	55
Water & Sediment, % vol, max.	D1796	0.05	0.05	0.05	0.05	0.50
Distillation Temperature, °C 90% % vol. Recovered	D86					
min			...	282 ^d	...	282 ^d ...
max			288	338	288	338...
Kinematic Viscosity, mm ² /S at 40°C	D445					
min			1.3	1.9	1.3	1.95.5
max			2.4	4.1	2.4	4.124.0
Ash % mass, max	D482	0.01	0.01	0.01	0.01	0.10
Sulfur, % mass, max ^e	D2622 ^f D129	0.05 ...	0.05
Copper strip corrosion rating max 3 h at 50°C	D130	No.3	No.3	0.50 No.3	0.50 No.3	2.00 ...
Cetane number, min ^g	D613	40 ^h	40 ^h	40 ^h	40 ^h	30 ^h
One of the following properties must be met:						
(1) Cetane index, min.	D976 ^{f†}	40	40
(2) Aromaticity, % vol, max.	D1319 ^f	35	35

TABLE 3
(continued)
ASTM D 975

DETAILED REQUIREMENTS FOR DIESEL FUEL OILS^A

Property	ASTM Test Method ^B	Grade Low		Grade No. 1-D		Grade No. 2-D		Grade No. 1-D ^C		Grade No. 2-D ^C		Grade No. 4-D ^C	
		Sulfur	No. 1-D	Sulfur	No. 1-D	Sulfur	No. 2-D	Sulfur	No. 1-D ^C	Sulfur	No. 2-D ^C	Sulfur	No. 4-D ^C
Cloud point, °C, max.	D2500	/	/	/	/	/	/	/	/	/	/	/	/
Ramsbottom carbon residue on 10% distillation residue, % mass, max	D524	0.15		0.35		0.15		0.15		0.35		...	

^A To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller and manufacturer.

^B The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 4.1.

^C Grades No. 1-D, No. 2-D and No. 4-D are required to contain a sufficient amount of 1,4-dialkyl amino anthraquinone (blue dye) so its presence is visually apparent.

^D When a cloud point less than -12°C is specified, the minimum flash point shall be 38°C, the minimum viscosity at 40° shall be 1.7 mm²/s and the minimum 90% recovered temperature shall be waived.

^E Other sulfur limits can apply in selected areas in the United States and in other countries.

^F These test methods are specified in CFR 40 Part 80.

^G Where cetane number by Test Method D 613 is not available, Test Method D 4737 can be used as an approximation.

^H Low ambient temperatures as well as engine operation at high altitudes may require the use of fuels with higher cetane ratings.

^I It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. However, satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6°C above the tenth percentile minimum ambient temperature for the area in which ambient temperatures for U.S. locations are shown in Appendix X2. This guidance is general. Some equipment designs or operation may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.

[†] Editorially corrected.

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Applicant's preferred diesel co-fuels contemplate low sulfur concentrations including those equal to or below 600, 500, 400, 300, 200, 150, 100, 60, 50, 45, 40, 30, 25, 20, 15, 10, 9, 8, 7, 6, 5, 2 ppm, or sulfur free. Preferred concentrations are 50 ppm or below.

Applicant's diesel co-fuels include those with low aromatic contents including those equal to or less than 60%, 50%, 47%, 45%, 40%, 35%, 30%, 28%, 25%, 22%, 20%, 18%, 15%, 12%, 10%, 7%, 6%, 5%, 4%, 3%, 2% by vol., or an aromatic free composition. Applicant prefers that 2 and 3 ring plus aromatics be excluded to the extent feasible.

Preferred fuels should be nitrogen free.

Applicant's diesel fuel cetane number include those equal to greater than 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90 or higher. Those in excess of 45, and 55 are preferred.

Applicant recognizes that an upper limit exists, if cetane is achieved solely via cetane additive enhancer(s).

It is desired that cetane be achieved via fuel formulation, to the extent possible. Thus, the desired fuel substituents would include n-paraffins, cyclohexane and benzene, in order of their preference. However, benzene concentrations should be strictly limited to less than 15, 10, 9, 8, 7, 6, 5.5, 5.4, 5.2, 5, 4.9, 4.5, 4.2, 4, 3.9, 3.7, 3.5, 3.5, 3, 2.5, 2, 1.5, 1.0, 0.5 volume percent (benzene free compositions are desirable), or limited to

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concentrations provided by regulation. Benzene concentrations of less than 5.0, 3.0, 2.5, 1.0, 0.5, 0.0 volume percent are preferred.

Polynuclear aromatics (PNA) should be reduced to
5 maximum extent possible and not exceed 7.0, 6.0, 5.0, 4.0, 3.0, 2.5, 2.0, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.2, 0.02, 0.01, 0.001 weight percent. PNA's less than 0.3 wt percent and/or compositions essentially free of polynuclear aromatics are most
10 preferred.

API should equal to or exceed 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 41.1, 42, 43, 44, 45, 45.4, 46.0, 47, 48, 49, 50.0, 51.0, 52.0, 53.0, 54.0, 55.0, or greater.

Densities should range from 800-820 kg/m³. Densities
15 outside this range are also desireable, including 780, 785, 790, 800, 805, 810, 815, 820, 825, 830, 840, 850 kg/mg³.

Substituent diesel fuel formulation, which operates to increase burning velocity and/or reduce combustion temperature is expressly contemplated, especially those
20 that operate to increase burning velocities 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, 5%, 8.0%, 10%, 15%, 20%, or more, over the clear or unadjusted fuel.

Formulation that increases laminar bunsen flame speed to 39, 40, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54,
25 55, 56, 57, 58, 59, 60, or greater, cm/sec is desired.

Similar formulation, which operates to reduce combustion temperature is contemplated, e.g. formulation that increases latent heat of vaporization equal to or

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above 30, 35, 38, 40, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 68, 70, 72, 74, 76, 78, 80 cal/gram, or greater, is desireable. It is an express embodiment that Applicant's diesel and diesel based compositions be constructed whereby latent heat of vaporization ("LHV") exceeds at least 40, 43, 45, 46, 50, 54 (100 BTU/lb), 56 cal/gram for heavy diesel, and 50, 53, 56, 59, 62, 64 (115 BTU/lb), 66, 68 cal/gram for light diesels.

As noted, it is an embodiment that Applicant's resultant reformulated fuel's latent heat of vaporization be higher than conventional or reformulated base diesel fuels, including low aromatic, low or now sulfur fuels, etc.

In the case of achieving maximum emission reductions, an acceptable minimum IBp temperature of a reformulated diesel fuel includes 356°F and a 95% distillation temperature of 545°F to 563°F max.

Example 86

A method wherein said an enhanced combustion vapor is combusted in a diesel engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 2.5 gr/gal, a diesel co-fuel base; wherein combined fuel is characterized as optionally having sulfur content not greater than 250 ppm, 200 ppm, 150 ppm, 100 ppm, 75 ppm, 50 ppm, 40 ppm, 30 ppm, 20 ppm, 10 ppm, 5 ppm, or being sulfur free; density ranging from about 880 to 800 kg/m³; viscosity

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ranging from 2.5 to 1.0 cSt at 40°C; cetane index of 40 to 70; an aromatic content by vol. ranging from approximately 0 to 35%, 0 to 20.0%, 0% to 15%, 0 to 10%, or less (inclusive 3-ring + aromatics not to exceed 0.16 vol%); a
5 T10 fraction temperature of about 190 to 230°C, a T50 fraction temperature of about 220 to 280°C, and a T90 fraction of about 260 to 340°C, and cloud point temperature of °C -10, -28, or -32 (or 6°C above tenth percentile minimum ambient temperature); a bunsen laminar burning
10 velocity of at least 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46 cm/sec, a latent heat of vaporization of at least 85, 90, 95, 90, 100, 105, 110, 115, 120 BTU/lb.

Example 87

15 A method where an enhanced combustion vapor is combusted in a diesel engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 2.5 gr/gal, a diesel co-fuel base; wherein combined fuel is
20 characterized as having an API range of about 41.1 to 45.4, optionally a sulfur content not exceeding 300, 250, 200, 150, 100, 50, 40, 20, 10, 5 wt ppm or sulfur free, absent nitrogen, and an aromatic content ranging from 0 to 5%, 1 to 10%, 0 to 15%, 0 to 20%, 0 to 35% by volume, PNA vol% of
25 0.03, 0.02, or less, a Cetane index greater than 45, an IBP of approximately 365°F, a 95% fraction ranging from 460°F to 540°F; a bunsen laminar burning velocity of at least 38 cm/sec, a latent heat of vaporization of at least 105

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BTU/lb; said method characterized in achieving reduced particulate emissions or improved fuel economy compared to co-fuel alone.

5 Example 88

Low emission diesel fuels comprising; a maximum sulfur concentration of no greater than 1100 ppm, 800 ppm, 440 ppm, 300 ppm, 250 ppm, 200 ppm, 150 ppm, 100 ppm, 50 ppm, 10 ppm, 5 ppm, or less (including sulfur free); density
10 kg/m³ of 800, 805, 810, 814, 815, 839, 840, or higher; viscosity of cSt at 40°C 1.8, 2.4, 2.5, or lower; cetane index of 46.2, 51.2, 52.1, 53.5, 57.5, 57.8, or higher; aromatics by vol.% 27.1, 2.45, 14.5, 1.1, 21.6, or lower, (including 3-ring + aromatics of 0.16, 0.02, or less); a
15 distillation fraction where, °C IBP ranges from 188.5, 213, 153, 215, 195, less than 180, and at T10 fraction temperatures range from 221, 215.5, 198, 227, 210, at T50 fraction temperatures range 272.5, 247.5, 249, 249, 227, and at T90 fraction temperatures range from 321, 272.5,
20 less than 285, 336, 271, 273, and at FBP temperatures ranges 348.5, 299, 360, 285, 300; cloud point °C -10, -28, -32; CFPP °C -11, -34, -34; caloric value, Mj/kg 42.8, 43.3, 43.3; optionally a burning velocity improving and/or combustion temperature reducing amount of an ECS compound;
25 optionally a combustion improving amount of a metallic; optionally a bunsen laminar burning velocity is at least 37, 40, 42, 45, 47 cm/sec, or higher (or alternatively, having a burning velocity higher than the base conventional

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or reformulated diesel); and wherein the latent heat of vaporization is in excess of 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130 btu/lb.

5 Example 89

 A reformulated diesel fuel comprising a diesel composition, wherein API ranges 41.1 to 45.4, sulfur does not exceed 10 wt ppm (preferably sulfur free), absent nitrogen, aromatics at 20, 15, 10, 5.0% vol or less, PNA
10 vol% 0.02 or less (preferably PNA free), Cetane index 45, 47, 50, 55, an IBP of 365°F, a 95% fraction @ 545°F, 525°F, 500°F, 475°F, or more; a combustion improving amount of a manganese or other metallic compound.

15 Example 90

 A liquid fuel comprising DMC at 0.01% to 5.0% by weight % oxygen (more preferably 0.5% to 2.5%) and at least one manganese metallic representing 0.001 to 2.8 gr/gal (preferably 0.065 to 1.0 gr/gal, most preferably 0.1 to 0.5
20 gr/gal), and a diesel co-fuel base; wherein combined fuel is characterized as having sulfur content not greater than 250 ppm, 100 ppm, 50 ppm, 5 ppm, or being sulfur free; density ranging from 880 to 800 kg/m³; viscosity ranging from 2.5 to 1.0 cSt at 40°C; cetane index of 40 to 60; an
25 aromatic content by vol. ranging from approximately 0 to 20.0%, (inclusive 3-ring + aromatics not exceeding 0.16 vol%); a T10 fraction temperature of about 190 to 230°C, a T50 fraction temperature of about 220 to 280°C, and a T90

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fraction of about 260 to 340°C, and cloud point temperature of °C -10, -28, or -32; a bunsen laminar burning velocity of at least 34 cm/sec, a latent heat of vaporization of at least 95 BTU/lb.

5

Example 91

A liquid fuel comprising DMC at 0.01% to 5.0% by weight % oxygen (more preferably 0.5% to 2.5%) and at least one manganese metallic representing 0.001 to 2.8 gr/gal (preferably 0.065 to 1.0 gr/gal, most preferably 0.1 to 0.5 gr/gal), and a diesel co-fuel base; wherein combined fuel is characterized as having an API range of about 41.1 to 45.4, a sulfur content not exceeding 10 wt ppm (preferably sulfur free), absent nitrogen, and an aromatic content of 0 to 20% by volume, PNA vol% of 0.02, or less, a Cetan index greater than 45, an IBP of 365°F, a 95% fraction ranging from 460°F to 540°F; a bunsen laminar burning velocity of at least 36 cm/sec, a latent heat of vaporization of at least 100 BTU/lb.

20

Example 92

The example of 91, additionally comprising a burning velocity increasing and/or temperature reducing ECS compound in concentration of 0.5 to 1.0, 0.5 to 1.2, 0.5 to 1.3, 0.5 to 1.5, 0.5 to 1.8, 0.5 to 2.0, 0.5 to 2.2, 0.5 to 3.0, 0.5 to 3.5, 0.5 to 4.0, 1.0 to 3.0, 1.0 to 5.0, 1.0 to 7.0, 2.0 to 8.0 volume percent oxygen in the composition.

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Example 93

The example of 91, 92, additionally comprising a combustion chamber deposit control/reducing additive, and optionally an injector or intake valve deposit control
5 additive.

Thus, it is an embodiment to incorporate an ECS fuel and a diesel co-fuel, such that the resultant fuel meets ASTM, industry and/or government specifications, present and future. In the practice of this invention, Mn or
10 metallic operating ranges in the resultant diesel composition may range from 0.001 to about 10.00 gr Mn/gal, 0.001 to 7.0, .001 to 5.0, .001 to 4.0, 0.001 to 3.5, 0.1 to 2.6, 0.1, 2.2, 0.1 to 2.0, 0.1 to 1.9, 0.1 to 1.6, 0.1 to 1.4, 0.1 to 1.2, 0.1 to 1.0, 0.1 to 0.9, 0.1 to 0.7, 0.1
15 to 0.5, 0.001 to 0.375, 0.1 to 0.25, 0.1 to 0.18, 0.001 to 0.125, 0.1 to 0.0625 Mn/gal, or equivalent, if an alternative metallic compound is employed (including combination).

It appears optimum Mn levels are less than 5 gr./gal, with those less than 3.0 or even 2.5 gr. Mn/gal being
20 acceptable. However, concentrations greater than 10, 12, 15, 20, 22, 25, 26, 27, 28, 29, 30, 31, 32, 35, 40, 50 grs Mn/gal are also contemplated, particularly in advance applications. For purposes of improving combustion, a
25 desireable concentrations include 0.03125, 0.0625, 0.09375, 0.125, 0.15625, 0.21875, 0.25, 0.28125, 0.3125, 0.34375, 0.375, 0.5, 1.0, 1.5, 2.0, 2.2, 2.3, 2.5, 2.7 gr Mn/gal, including concentrations within these ranges. Desireable

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ranges includes from about 0.001 to about 3.00, 0.001 to 2.9, 0.001 to 2.8, 0.001 to 2.7, 0.001 to 2.6, 0.001 to 2.5 gram Mn/gal. Ranges outside these are acceptable.

Other manganese concentrations include those equal to
5 or greater than 0.015625, 0.03125, 0.0625 0.125, 0.25,
0.275, 0.375, 0.50, 0.625, 0.75, 0.875, 1.0, 1.125, 1.25,
1.375, 1.5, 1.625, 1.874, 2.0, 2.125, 2.25, 2.375, 2.5,
2.625, 2.75, 2.875 gram Mn/gal. A desireable range includes
from about 0.001 to about 1.50 gram Mn/gal. Other
10 desireable ranges include from about 0.001 to about 0.50
gram Mn/gal of composition. Lower concentration ranges from
.001 to about 0.25 grams/gal are also contemplated. Ranges
greater than 0.0625 gr Mn/gal are also contemplated.

However, as noted above, the greater the O₂
15 concentrations contained in the fuel composition,
especially with superior ECS compounds, the greater the
permissible Mn concentrations. Also with heavier fuel
compositions, which enjoy improve burning velocities and/or
reductions in combustion temperature, manganese
20 concentrations may be increased.

Often, manganese concentrations must exceed 1/64,
1/32, 1/16, 3/32, 1/8, 5/32, 7/32, 1/4 gr Mn/gal prior to
noticable improvement in fuel economy or power.

A synergism occurs complimenting the usage of ECS
25 compounds and Mn, particularly when T-90 temperature are
reduced. Differing fuel specifications, operating
conditions, environmental requirements, and combustion
systems will dictate final compositional construction.

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Applicant notes the desirable oxygen of his ECS component by weight in diesel compositions, which yields good results normally exceeds at least 1.0% by weight, and those equal to or exceeding 1.5%, 1.75%, 2.0% are desireable. However, in the practice of this invention lower O₂ concentrations are contemplated, including to a low as 0.01 weight percentage.

In the practice of this invention oxygen concentrations ranging from 0.01 to 0.5% weight are acceptable. Oxygen concentrations from 0.01 to 1.5% weight percent is desireable. O₂ concentrations from about 0.5 to 5.0%, and those greater than 1.5% slightly more preferred. Other oxygen ranges include 0.5 to 1.0, 0.5 to 1.2, 0.5 to 1.3, 0.5 to 1.5, 0.5 to 1.8, 0.5 to 2.0, 0.5 to 2.2, 0.5 to 3.0, 0.5 to 3.5, 0.5 to 4.0, 1.0 to 3.0, 1.0 to 5.0, 1.0 to 7.0, 2.0 to 8.0 volume percent oxygen in the composition.

Acceptable oxygen ranges, when the ECS fuel constitutes a significant minority or substantially greater percentage of the composition includes oxygen weight concentrations of 5.0%, 10%, 15%, or 20%, or greater. In larger diesel fuel engines, including locomotive, marine and large stationary industrial applications, it is anticipated that the fuel compositions will contain O₂ concentrations of 2%, 3%, 5% weight, or more.

There are no maximum limit anticipated in advanced applications. Hence, in the practice of this invention, O₂ concentrations maximizing the advantages of Applicant's

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invention are expressly contemplated, especially those that maximize advance combustion of the metallic.

Applicant has unexpectedly discovered that diesel emissions, including particulates, HC, CO and NOx emissions are materially reduced in the practice of Applicant's invention. Combustion chamber deposits, absent additives are also reduced. Such reductions appear to be closely tied to the invention's increases in burning velocities and reductions in combustion temperatures.

Applicant has also unexpectedly discovered that due to increases in burning velocities and lower combustion temperatures that diesel engine noise can be controlled, without sacrificing economy and emissions.

The properties of commercial distillate diesel fuels depend on the refinery practices employed and the nature of the crude oils from which they are derived. Thus, they may differ both with and within the region in which they are manufactured. Such fuels generally boil over a range between 163 and 371°C (325-700°F). Their makeup can represent various combinations of volatility, ignition quality, viscosity, sulfur level, gravity, and other characteristics.

The properties and preferred practice of Applicant's diesel co-fuels are set forth in International Application No. PCT/US95/02691.

Applicant's preferred diesel co-fuels enjoy high cetane numbers, especially those exceeding 40 cetane, and

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can be produced where aromatics are converted to naphthalenes and paraffins.

The diesel co-fuels of Applicant's invention include all ASTM grades, including Grade low sulfur No. 1-D, which is a special purpose, light distillate fuel for automotive diesel engines requiring low sulfur fuel and requiring higher volatility than that provided for Grade low sulfur No 2-D, and is met to comply with 40 CFR Part 80 regulations. Grade Low Sulfur No. 2-D, which is a general purpose middle distillate fuel for automotive diesel engines requiring low sulfur fuels. It is also suitable for use in non-automotive applications, especially in conditions of varying speed and load. This grade is also in conformity with 40 CFR Part 80 regulations. Grades No. 1-D and No. 2-D, which are similar in purpose to their low sulfur counter parts, except that their sulfur contents are not as strictly regulated. Grade No. 4-D, which is a heavy distillate fuel, or a blend of distillate and residual oil, for low and medium speed diesel engines in non-automotive applications involving predominately constant speed and load.

Type C-B - Diesel fuel oils for city-bus and similar operations

Type T-T - Fuels for diesel engines in trucks, tractors, and similar service. Type R-R - Fuels for railroad diesel engines

Type S-M - Heavy-distillate and residual fuels for large stationary and marine diesel engines.

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It is anticipated the base co-fuel hydrocarbon composition of Applicant's diesel co-fuels will be tailored to maximize the beneficial aspects of ignition quality, heating value, volatility, gravity, oxidation stability, burning velocity, latent heat of vaporization, etc., to positively effect combustion, power, economy, emissions, fuel economy, wear, deposit formation, starting, warm starting, driveability, noise, particulate generation and smoke performance of Applicants diesel engines.

In the practice of this invention a cetane number of 30 is desireable. A cetane number of 40 or greater is preferred, especially in low sulfur No. 1-D and low sulfur No. 2-D fuels. An optimal cetane number in the practice of this invention is greater than 48. However, in advanced reformulated diesel fuels cetane numbers greater 50, 55, 60, 65, 70, 75, 80 are contemplated. It is also a preferred practice, when employing low sulfur diesel fuels Grade No. D-1 and No. D-2 to have a minimum cetane index number, a limitation on the amount of high aromatic components, of 40 (as measured by ASTM D 976) or an aromatic content not exceeding 35% by volume (as measure by ASTM D 1319).

Example 94

A composition comprising a diesel fuel meeting ASTM 975 specifications (or fuel oil, aviation turbine, or gas oil) a combustion improving amount of dimethyl carbonate, a co-solvent, and a cyclopentadienyl manganese tricarbonyl

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compound having a concentration ranging from about 0.001 to about 2.5 gr Mn per gallon; whereby resultant fuel combustion results in improved thermal efficiency and/or fuel economy, and meets minimum flash point temperatures..

5

Example 95

A No. 2 diesel fuel composition comprising a minor portion of a combustion improving amount of dimethyl carbonate and a cyclomatic manganese tricarbonyl, and a major portion of a base diesel fuel, such that resultant fuel has a cetane of 42 to 50 (preferably substantially greater), an aromatic content of less than 28 volum percent (preferably less than 20%, more preferably 15%, most preferably less than 10%), a T-90 temperature of 560°F to 600°F (more preferably less than 540°F, 520°F, 500°F or lower), a sulfur content of 0.08 to 0.12% mass (more preferably 0.05% or sulfur free), an API gravity of 32 to 37 (more preferably higher), and a minimum flash point of 130°F (optionally obtained via use of co-solvent or salt).

20

Example 96

A No. 1 diesel fuel composition containing a minor portion of a combustion improving amount of dimethyl carbonate and a cyclomatic manganese tricarbonyl, and a major portion of a base diesel fuel, such that resultant fuel has a cetane of 48 to 54 (preferably substantially greater), aromatics representing 10% or less by volume, a T-90 temperature of 460°F to 520°F (more preferably less

25

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than 425°F, or lower), a sulfur content of 0.08 to 0.12% mass (more preferably less than 0.05% mass), API gravity of 40 to 44 (more preferably higher), and a minimum flash point of 120°F.

5

Example 97

The above examples, wherein fuel meets ASTM D 975 specifications.

10

Example 98

A method for operating a diesel engine, said method comprising injecting the fuels of examples of 88-90 (including a substituted No. 5-heavy) by means of high pressure direct fuel injection system, employing pressures ranging from 30 MPa to 120 MPa, wherein the average vapor particle size is less than 70, 60, 40, 30, 20, 10, 5 microns, more preferably 40-60 microns; whereby burning velocity is increased.

20

Example 99

The methods above, wherein the combustion system additionally comprises a turbocharger, an ERG system, and wherein the fuel injection system employs sensor input means to regulate fuel injection rate and/or timing.

25

Example 100

A method incorporating the above Examples, wherein

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an engine is operated under a moderate to heavy load, of at least 16, 17, 18, 20, 22, 24, 28, or more, ihp (employing equivalent of 180hp to 280 hp engine); whereby fuel economy is improved.

5

Example 101

The method examples above, wherein resultant exhaust emissions meet U.S. EPA and Clean Air Act regulations, including 42 USC 7545 et seq.

10

In the practice of this invention ignition promoters may be employed, individually and/or in combination with ECS compounds, particularly in fuels which require higher temperatures to ignite, which extends their period of ignition. Such promoters include di-tertiary butyl peroxide, alkyl peroxides, alkyl hydroperoxides, alkyl nitrate additives, including ethyl-hexyl nitrate and iso-propyl nitrate, 2,5 dimethyl 2,5 di(tertiary butyl peroxy) hexane, tertiary butylcumyl peroxide, di(tertiaryamyl) peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, and mixtures thereof.

15

20

Example 102

A low emission No. 2 grade diesel fuel comprising a minimum cetane number of 52, maximum fuel sulfur of 350 ppm (more preferred less than 0.05% mass), aromatics less than 30% volume (more preferably less than 15%), a combustion improving amount of dimethyl carbonate and a combustion

25

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improving amount of a cyclomatic manganese tricarbonyl compound.

Example 103

5 A low emission diesel fuel comprising a minimum cetane number of 52, maximum fuel sulfur less than 100 ppm, aromatic content of 12%, T-90 temperature of 475°F, bromin number of 0.10, a combustion improving amount of dimethyl carbonate ranging from 0.5 to 4.0% oxygen by weight, and a
10 combustion improving amount of a cyclomatic manganese tricarbonyl compound.

Example 104

 A low emission diesel fuel comprising a minimum cetan
15 number of 62, maximum fuel sulfur less than 0.01% weight, 10% aromatic content, olefin by weight less than 30%, 25%, 20.0%, 15.0%, 10%, 7.0%, 6.0%, 5.0%, 4.0%, 3.0%, or less, including olefin free, T-90 temperature of 514°F, bromine number of 0.10, aniline point less than 145°F, a combustion
20 improving amount of dimethyl carbonate and/or optionally triethylene glycol or tetraethylene glycol; and a combustion improving amount of a cyclomatic manganese tricarbonyl compound.

25 Example 105

 The composition of Example 104, wherein said composition is combusted in a heavy duty truck engine and

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HC, CO, NOx, and particulate emissions are 1.3, 15.5, 4.0, 0.10 gm/bhp-hr, respectively.

It is an embodiment of this invention that the emissions of Applicant's fuels, ASTM, CAA, CARB, Swedish/European, and all international requirements and/or other governmental regulations, current and future.

[TABLE 4 INTENTIONALLY OMITTED]

10 An additional embodiment is the reduction of PM 10 (particulate matter of 10 microns or more), which is believed to be caused by heavier aromatics. It is also an embodiment to reduce particulate matter to 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0 microns or lower. Applicant's invention
15 is particularly effective to reducing such particulate matter.

Example 106

A method of operating a diesel engine, comprising:
20 introducing into the combustion chamber via direct fuel injection under pressure, an atomized ECS compound of sufficiently high burning velocity and latent heat of vaporization, together with a combustion improving metallic, and a reformulated diesel co-fuel; combusting
25 said fuel at extremely high efficiency and rate, whereby particulate combustion emissions are substantially avoided, and if formed are gaseous submicron particles of high kinetic energy.

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In the practice of this invention all fuels and co-fuels are contemplated to be combusted in engines employing as required advanced lubricating oils and technologies, as an additional means for reducing combustion temperatures and increasing burning velocities.

Contamination of lubricating medium can cause or advance combustion chamber and/or other deposits. The elimination of combustion chamber deposits (CCD) is an express object of Applicant's invention, as said CCD interfere with combustion an increase combustion temperature, in turn exasperating NOx emissions and the like.

Thus, advanced lubricating oils, designed to avoid such contamination and/or designed to improve lubricity under accerlerated combustion is expressly contemplated.

Non-limiting examples of contemplated lubricating oils include those meeting API CG-4, API CF-4/SG, API CF-4/SH, future PC-7 standards, SAE J300, and/or other standards that operate to minimize piston deposition on operation with low/no sulfur fuels. It is known that piston deposition operates to increase other deposits and hazardous emissions and therefore should be avoided.

Other advanced lubrication technologies, such as those disclosed in U.S. Patent #4,204,968, #3,001,941 which improves combustion efficiency and/or burning velocity (noted by increases in fuel economy), and/or which tend to reduce operating temperatures are also contemplated in the various aspects of this invention.

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See International Application No. PCT/US95/02691 for analysis of Example tests and Figures 1 to 7, incorporated herein by reference.

5 [TABLE 5 INTENTIONALLY OMITTED]

FIGURE 8

Figure 8 shows technical enleanment of oxygen containing fuels, which have not been adjusted to elevate depressed T-15 to T-70 regions. As Applicant disclosed in his 770,836 Application, lower molecular weight alcohols and ethers depress distillation temperatures due to azeotrophing effect and adversely impact warm driveability, particularly warm engine start up.

15 Figure 8 shows that by adjusting distillation curve, preferably by tailoring underlying hydrocarbon base, or by the addition of higher molecular weight co-solvent, particularly C4, C5, C6 plus alcohols, while maintaining a constant level of oxygen, that an adjusted distillation curve can be achieved, which is above the technical enleanment region. Hence capable of avoiding warm operational driveability problems.

Applicant notes the addition of higher molecular weight hydrocarbon material boiling above 220°F, 250°F, 270°F, 300°F, 320°F, 370°F, and therewithin, can be added to the fuel to elevate noted depression. It is normally desirable, while not required, that said hydrocarbon

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material have some aromaticity and/or azeotrophenic property.

Thus, Figure 8 shows that tailoring of the base hydrocarbon fuel, wherein a hydrocarbon fraction elevates T-60 to T-70 or higher distillation temperature, can be compressed into the mid-range fractions, due to addition of C1 to C3 alcohols and MTBE or ETBE. Thus, the higher molecular weight hydrocarbons elevating T-60, T-70 plus fractions are offset by MTBE, ETBE and C1 to C6 alcohols, which depress the T-20 to T-50 fractions.

GASOLINE COMPOSITIONS

See International Application No. PCT/US95/02691 for additional practice disclosure on gasoline compositions.

Automotive gasolines contemplated in Applicant's invention include conventional unleaded, reformulated unleaded, low RVP fuels, low sulfur, no sulfur gasolines, low octane gasolines, moderate octane gasolines, high octane gasolines, advanced atomization, vaporization, injector volatilization gasolines, and the like, and/or any gasoline meeting ASTM and/or other regulatory standard, existing and future, and combinations thereof.

Non-limiting examples of the gasoline engine/fuel systems include, carburetor, improved gasoline, manifold feed/injected, direct injection, direct injected stratified charge, advanced stratified charge, and the like. It is contemplated that Applicant's automotive gasolines will be in combustion systems employing exhaust catalysts

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(including three way systems), regulated emission control systems, and the like.

One of the particular objects of Applicant's invention is the incorporation of emission catalysts, OBD II catalyst efficiency monitors, related emission control systems in methods, where upon their operation in the presence of a Mn containing combustion exhaust gas, is not impaired.

Another object is the operation of gasoline engines operating under minimum threshold loads, where upon the benefits of Applicant's invention become beneficial. For example, Applicant has discovered that when employing ECS compounds and minor amounts of metallic, e.g. Mn, that optimum fuel economy and temperature reduces do not start to occur until loads are at least 12.5 ihp to 16.0 ihp.

An object of instant invention is to employ and make gasolines having superior combustion, emission and operational features with a very wide range of octane value $(R + M)/2$, s, including extremely low (e.g. 5 to 30, 10 to 35, 15 to 40), to low (e.g. 40 to 60, 50 to 70, 60 to 75), to moderately low (e.g. 75 to 80, 75 to 85), to average (85 to 88, 86 to 90), to high (e.g. 90 to 95, 93 to 100, 95 to 105) to extremely high 105 to 115, or higher.

Another object of this invention is improved combustion of gasolines and the operation of internal combustion engines at altitude. At altitudes above sea level, particularly those greater than 1,500, 2,000, 2,500, 3,000, 3,500, 4,000, 4,500, 5,000, 5,500, 6,000, 6,500, 7,000, 7,500, 8,000, 8,500, 9,000, 9,500, 10,000, 10,500,

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11,000 feet above sea level in combustion in gasoline and diesel engines show incomplete combustion and elevated CO, particularly in older engines.

5 It is still another object to employ faster burning velocity, higher LHV ECS compounds (e.g. DMC, methanol, ethanol) with lower burning velocity LHV ECS compounds (e.g. MTBE, ETBE), especially in circumstances where the later compounds have long photooxidation periods, due not readily decompose, and are suspected as being carcinogenic.

10 Employing Applicant's fuel compositions and method at altitudes wherein atmospheric pressures are reduced on the order of 0.5 psi to 8.0 psi, 0.5 to 1.0 psi, 0.5 to 2.0 psi, 0.5 to 3.0 psi, 0.5 to 2.5 psi, 0.5 to 3.5 psi, 0.5 to 4.0 psi, 0.5 to 4.5 psi, 0.5 to 5.0 psi, 0.5 to 5.5 psi,
15 0.5 to 6.0 psi, or more, effectively enhances combustion, whereby reducing the emissions of incomplete combustion, including CO, particulates, hydrocarbons, NOx, etc., especially CO emissions which are otherwise elevated compared to clear fuel at sea level.

20

Example 157

A method of operating an internal combustion engine at an altitude exceeding 1,000, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 9,000, 10,000, or more feet above sea
25 level and/or wherein atmospheric pressure is 0.5 to 8.0 psi below that of sea level, said method comprising: mixing an ECS and metallic containing gasoline or diesel co-fuel; wherein resultant fuel has an increased burning velocity

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and/or reduced combustion temperature (.g. compared to clear co-fuel or an MTBE containing co-fuel); injecting resulting fuel into combustion chamber of said engine, wherein ambient pressure is 0.5 to 8.0 psi below sea level; 5 combusting said fuel; wherein CO and/or other emissions associated with incomplete combustion due to lower ambient pressure are reduced (e.g. over clear fuel combusted at same altitude).

An additional object of this invention is the improved 10 combustion, decomposition and general deposition of MTBE and/or other known carcinogenic ethers into more benign or benign compounds, as to avoid contamination of ground and surface water.

Applicant has discovered that certain high octane 15 ethers, namely MTBE and ETBE, are found in high relative concentrations in the evaporative and/or combustion exhaust emissions of MTBE or ETBE containing fuels. The increase of said compounds into air and water supply, especially at altitude, now constitutes the begining of a major hazard.

20 Applicant has discovered MTBE to be rather stable once emitted into the atmosphere, and appears to be rather solubility in atmospheric water vapor. Thus, MTBE as a fuel component is now and will continue to be found in ever increasing concentrations in ambient air and ground water, 25 constituting a potential hazard, due to its carcinogenic attributes. Thus, a need exists to enhance the decomposition of MTBE combustion to reduce total ambient concentrations of MTBE in the atmosphere.

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Applicant has discovered that by employing a combustion accelerating ECS compound, especially one whose burning velocity and/or heat of vaporization is greater than MTBE's, especially an ECS compound releasing high amounts of free radicals, and optionally together with at least one combustion improving amount of a metallic (e.g. Shell Chemical's SparkAid or a potassium salt and/or a manganese compound or other useful metallic), in combination with an MTBE or ETBE containing fuel, the MTBE/ETBE containing fuel enjoys better combustion and MTBE decomposes at an accelerated rate, compared to MTBE containing fuel alone.

Example 108

An ameliorative fuel composition characterized as an aviation/automotive gasoline, diesel, turbine, fuel oil, or other fuel containing MTBE, ETBE, TAME, or mixture; said fuel additionally containing a combustion improving amount of an ECS compound (preferably DMC) having a burning velocity and/or a latent heat of vaporization greater than MTBE; and optionally a combustion improving amount of at least one metallic; whereby enhanced attributes of combustion accelerate decomposition of carcinogenic ether prior to its emission into atmosphere.

Example 109

A method of 108 reducing potentially carcinogenic ether concentrations from atmosphere; said method

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comprising combusting an MTBE containing fuel in combination with DMC and optionally a combustion improving metallic.

5 Example 110

A fuel composition of Example 108, wherein the fuel is a reformulated gasoline and contains MTBE, ETBE, TAME, or mixture, said ether or mixture comprising an amount equal to or less than 2.7, 2.5, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 10 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3 weight percent oxygen of the fuel; and a ECS compound having a burning velocity and a heat of vaporization greater than said ether and a minimum oxygen weight content of at least 0.02%, such that total fuel 15 oxygen by weight is less than 6.0%, 5.0%, 4.0%, 3.7%, 3.0%, 2.7%, 2.5%, 2.2%, 2.0%, 1.9%, 1.5%, 1.2%, 1.1%, 1.0%, or less; and optionally, a combustion improving amount of at least one metallic compound.

20 Example 111

An improved MTBE fuel composition comprising: a low or no sulfur hydrocarbon base fuel, MTBE, and an ECS compound having a burning velocity greater than MTBE (preferably 20%, 30%, 40%, 50%, 60%, or more, with DMC preferred), 25 wherein total oxygen by weight of the fuel does not exceed 8.0%, 6.0%, 5.0%, 4.5%, 4.0%, 3.7%, 3.5%, 3.0%, 2.7%, 2.5%, 2.25%, 2.2%, 2.0%, 1.9%, 1.8%, 1.5%, 1.2%, 1.1%, 1.0%, 0.8%, 0.7%, 0.5%; and a burning velocity improving amount

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of a metallic, including a potassium salt marketed by Shell Chemical Corporation known as SparkAid; and/or optionally an anti-knock or combustion improving amount of a manganese metallic compound (in lieu of or in addition to the potassium salt).

Example 112

The Composition of Example 111, wherein the fuel composition is unleaded, containing less than 400, 350, 300, 250, 200, 150, 100, 50, 40, 30, 20, 10, 5, 0 ppm sulfur, and comprised of 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10 parts oxygen/or parts MTBE (or parts MTBE/ETBE/TAME and mixture) to part ECS compound; and/or wherein the metallic concentration of metallic potassium or potassium salt is less than 3.0, 5.0, 6.0, or 1.0 to 4.0, 1.0 to 10.0, 2.0 to 15.0, 2.0 to 20.0, 3.0 to 30.0, 4.0 to 35.0, or greater, ppm of the fuel; and/or wherein the manganese concentration is at least 1/64, 1/32, 1/16 gram Mn/gal of the fuel composition.

Example 113

A method employing the fuel compositions of 111, wherein said composition is supplied to and combusted in a spark-ignited internal combustion engine, wherein MTBE emissions are reduced by 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, or more, compared to same fuel

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containing same concentration of MTBE, absent ECS compound and metallics.

Another object is a combustion metallic containing gasoline absent an oxygenate, which has improved burning velocity and/or reduced combustion temperatures. Thus, Applicant's invention includes fuel compositions, wherein combustion burning velocities are increased over typical base compositions. This may be accomplished by formulating a co-fuel composition to include hydrocarbon substituents having increased burning velocities, and/or by including combustion catalysts or combustion improving metallics such as Shell's potassium salt.

Example 114

A combustion composition comprising: an low or no sulfur gasoline or diesel co-fuel; constructed to have increased burning velocities over typical base fuel; and an organ-manganese compound; and optionally a burning velocity improving amount of additional metallic.

Example 115

The composition of Example 114, wherein constructed/reconstructed co-fuel has a burning velocity at least 2.0%, 3.0%, 5.0%, 7.5%, 9.0%, 10%, 12%, 15%, 17%, 20%, 25%, 30%, 40%, 50%, or 60% or higher than unmodified base fuel; and a manganese concentration exceeding or equal to 1/128, 1/64, 1/32, 1/16, 3/32 gr Mn/gal; and wherein said fuel optionally contains a burning velocity amount of

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a combustion acceleration amount of separate metallic, preferably a potassium salt in a concentration not exceeding 25, 20, 18, 16, 14, 12, 10, 8, 7, 6, 5, 4, 3, 2, or 1 ppm (metallic or metallic compound); and the composition optionally contains means of reducing combustion temperature (as set forth in the specification herein), but not limited to distillation modification and/or employing a combustion chamber deposit control additive in a concentration of 50 to 400, 100 to 600, 150 to 800, 150 to 1000, 200 to 1500 mg/kg or other amount sufficient to avoid combustion chamber deposits; whereby combustion temperatures are reduced.

Applicant's co-fuel gasolines should be constructed to minimize hazardous pollutants to the maximum extent possible. Thus, sulfur concentrations should approach sulfur free levels, if possible, harmful heavy aromatics (while their effect is substantially mitigated in the practice of this invention) should be reduced as much as practical. To the extent possible, co-fuels should be formulated to reduce volatile organic compounds (VOC's), NOx, benzene, butadiene, formaldehyde, acetaldehyde, polycyclic organic material. Reformulated gasolines constructed under the complex model are expressly contemplated.

An important embodiment of Applicant's invention is its capacity towards ultra clean combustion emissions, due to the nature of its combustion. Consequently, in addition to the reduction of most hazardous emissions, it is an

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embodiment to avoid combustion chamber deposits, which now be caused by the use of detergents to keep intake valves clean.

5 An additional embodiment is the reduction of PM 10 (particulate matter of 10 microns or more), which is believed to be caused by heavier aromatics. It is also an embodiment to reduce particulate matter to 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.25 microns or lower. Applicant's invention is particularly effective to reducing such particulate matter (PM) in both 10 gasolines and fuels heavier than gasolines (e.g. diesel).

Example 116

A method of reducing the size of particulate matter incorporating an ECS/metallic fuel composition in 15 combination with a co-fuel, preferably a co-fuel equal to or heavier than gasoline, wherein said fuel is combusted in an engine; emitting combustion emissions from said engine, whereby particulate matter is less than 10 PM, 5 PM, or 2.5 20 PM; and particulate emissions are reduced compared to co-fuel, absent ECS/metallic fuel.

Example 117

The method of Example 116, wherein the fuel 25 composition contains aromatic concentrations of 30%, 27%, 25%, 22%, 20%, 19%, 18%, 17%, 16%, 15%, or less by vol.

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Example 118

A conventional or reformulated unleaded fuel composition comprising: sulfur at less than 300, 250, 200, 150, 100, 60, 50, 20, 10, 5 ppm, including range of 5 ppm to 50 ppm or 15 to 25 ppm sulfur or sulfur free; a polynuclear free aromatic concentration of less than 50%, 45%, 40%, 35%, 30%, 27%, 25%, 22%, 20%, 18%, 16%, 15%, 12%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, or less, by volume, including ranges therein, or aromatic free composition; a none C4 to C5 olefinic concentration less than 20%, 15%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1% including range of 3.0% to 5.0% by volume (also including olefin free concentrations); a benzene concentration of 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1.0% volume, or less, including benzene free compositions; an RVP of less than 12.0, 11.5, 11.0, 10.0, 9.0, 8.5, 8.0, 7.5, 7.0, 6.9, 6.5, 6.0, 5.5 psi and ranges of 11.5 to 12.0 psi or 6.5 to 6.9 psi; oxygen at 0.5% to 5.0% or 3.7% wt., 0.6 to 3.0% wt, 0.7% to 2.7% wt., 1.8% to 2.2% weight, provided in part or wholly by at least one ESC compound (preferably DMC); a combustion improving amount of at least one metallic, including a cyclomatic manganese tricarbonyl having an Mn concentration of 1/128 to 3/8 gr./gal (1/128 to 1/8 preferred) or up to 1/64, 1/32, 1/16, 1/8, 1/4, 3/8; at least one combustion enhancing deposit control additive selected from combustion chamber deposit control, port fuel injector, intake valve deposit control additive, and mixture; and wherein said composition has a driveability

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index less than 1120, 960 (less than 930 preferred); whose t-50 mid range temperature exceeds 170°F, 175°F (preferably ranging from 190°F to 210°F); whose T-10 temperature is less than 160°F (preferably less than 140°F, 120°F); and wherein
5 the composition has an average latent heat of vaporization equal to or greater than 130, 135, 140, 145, 150, 155, 160, 165 btu/lb or alternatively greater than 860 btu/gal (preferably greater than 900, 910 btu/gal); and wherein the composition optionally has a minimum laminar bunsen flame
10 burning velocity of 40, 43, 45, 48, 50, 60, 65, 70, 75, 80, 90 cm/sec (preferably 45, 48, 50, 60 cm/sec., or greater are preferred).

Example 119

15 The vapor composition of method Example 118, absent metallic.

Example 120

A method of operation an internal gasoline combustion
20 engine, said method comprising: mixing a convention, non-convention, or reformulated gasoline with a combustion improving amount of an ECS compound and a combustion improving amount of MMT and/or other metallic (including the fuel of Example (im abv); combusting said fuel in
25 said engine, wherein engine is under load of at least 12.5 ihp (more preferably at least 16.0, 20.0 ihp), wherein fuel economy is increased.

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Example 121

The method of 120, wherein the load is approximately 20 ihp and fuel economies are improved 0.5%, 1.0%, 2.0%, 3.0%, 5%, or 2.0% to 30%, and/or combustion temperature is reduced compared to conventional fuel, including temperatures from 2°F to 10°F, 5°F to 20°F, 10°F to 50°F, 15°F to 60°F, 20°F to 100°F, 25°F to 125°F, 25°F to 150°F, 50°F to 200°F, 25°F to 225°F, 25°F to 250°F, 50°F to 300°F, or mor .

It is another object of instant invention is improving burning velocity/combustion temperatures by modifying T-90 and/or end-boiling point distillation fractions enhancing combustion, improving mileage, driveability and/or reducing hazardous combustion emissions.

It is an object that Applicant's gasolines, including RFG, have a driveability index as defined by $(1.5 \times T_{10}) + (3 \times T_{50}) + (T_{90})$ of less than 1370, 1330, 1300, 1295, 1275, 1236, 1200, 1190, 1180, 1170, 1160, 1155, 1150, 1140, 1130, 1120, 1100, 1090, 1080, 1075, 1050, 1000, 975, 960, 950, 945, 940, 935, 930, 925, 920, 910, 900, 875, 850, 840, 825, 800, or less. It is preferred that T50 temperatures simultaneously equal or exceed 150, 155, 160, 165, 170, 175, 180, 185, 190, 195 degrees F. An acceptable T50 range includes 190 to 210 degrees F. It is also preferred that the T-10 distillation fraction be 160, 155, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 98, 96, 95, 94, 93, 92, 91, 90, 89, 88, 87, 85, 80 degrees F, or less. An acceptable T90 range includes 280 to 300 degrees F.

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Example 122

An unleaded reformulated gasoline composition whose driveability index is less than 1160, 1150, 1140, 1130, 1120, 1110, 1100, 1080, 1050, 1040, 1020, 1000, 995, 990, 985, 982, 980, 978, 975, 973, 970, 968, 967, 965, 964, 960, 950, 945, 940, 935, 930, 927, 925, 922, 920, 915, 910, 905, 900, 895, 890, 885, 880, 875, 870, 865, 860, or less; whose t-50 mid range exceeds 170°F, 175°F; whose t-10 is less than 130°F, 125°F, 120°F, 115°F, 110°F, 100°F, 95°F, 90°F, 85°F, 80°F, 75°F, 70°F; said composition containing a combustion improving amount of a metallic; a burning velocity improving and/or combustion temperature amount of an ESC compound;

15 Example 123

The unleaded reformulated gasoline of example (im abv), whose driveability index is less than 1120, 1050, 1000, 970, 940, 930; and whose T-10 temperature is 100°F to 90°F; RVP is 9.0, 8.7, 8.5, 8.2, 8.1, 8.0, 7.9, 7.8, 7.7, 7.6, 7.5, 7.3, 7.0, 6.9, 6.8, 6.7, 6.6, 6.5, 6.4, 6.2, 6.0, 5.9, 5.8, 5.6, or less;

Thus, it is an object to improve combustion by controlling mid-range distillation temperatures. Still another is T-10 adjustment to enhance combustion properties of this invention. RVP reductions, which are tied to reductions in T-10, are contemplated and it is preferred that Applicant's gasolines generally be lower RVP fuels 4.0

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to 12.0 psi, more preferred are those 4.0 to 9.0 psi, 4.0 to 8.0 psi, 4.0 to 7.5 psi, 6.0 to 7.0 psi, 6.0 to 6.5 psi, 1.0 to 6.0 psi, 1.0 to 3.0 psi, 1.0 to 2.0 psi, or lower. Contemplated RVP's include 5.0, 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8, 5.9, 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 7.8, 6.9, 7.0, 7.1, 7.2 (max), 7.3 (max), 7.4 (max), 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1 (max), 8.2 (max), 8.3 (max), 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 9.0 psi. Winter RVP's may range from 11.5 to 12.0 psi, or higher. Summer RVP's may range from 6.5 to 6.9 psi.

Example 124

The reformulated fuel composition of example 122, wherein t-10 temperature is less than 125°F, 120°F, 115°F, 110°F, 100°F, 95°F, 90°F, 85°F, 80°F; and RVP is 6.4, 6.5, 6.6, 6.7, 7.8, 6.9, 7.0, 7.1, 7.2 (max), 7.3 (max), 7.4 (max), 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1 (max), 8.2 (max), 8.3 (max), 8.4, 8.5 psi, or less.

In the T-10, T-50, T-90 temperature reducing or control practices of this invention, eliminating gasoline components having low latent heats of evaporation and/or low burning velocities is expressly contemplated.

It is preferred the finished hydrocarbon portion of the gasoline composition (e.g. absent oxygenates and metals, etc.), particularly reformulated fuels, including automotive and aviation gasolines, have an average latent heat of vaporization greater than 130 btu/lb or 830 btu/gal. More preferred are 135, 140, 145, 150, 155, 160,

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165, 170, 175, 180, 185, 190, 195, btu/lb, or greater, if practical.

Applicant has discovered compositional/ component substitution and/or modification leading to a higher latent heat of evaporation can be normally be accomplished absent losses in the fuel's heating. Often, heating values increase.

In the practice of this invention, it is acceptable that reductions of end point and/or T-90 temperatures be in such an amount that the average latent heat of evaporation of the adjusted fuel (e.g. the reduced fuel), such that its latent heat of vaporization is 0.5% to 10.0%, or greater, than the unadjusted base fuel. Increases of 1.0%, 2.0%, 3.0%, 4.0% to 20%, 5.0% to 25%, 6.0% to 40%, or greater, are also desireable.

In the preferred practice of this invention, Applicant has discovered that acceptable T-90 temperatures will range from 240°F, 250°F, 255°F, 260°F, 265°F, 270°F, 275°F, 278°F, 280°F, 285°F, 290°F, 292°F, 293°F, 294°F, 295°F, 296°F, 297°F, 298°F, 299°F, 300°F, 305°F, 310°F, 315°, 320°F, 325°F, 330°F, 335°F, 340°F, 345°, and ranges therein, including 280°F to 300°F, 265°F to 295°F. Temperatures outside these ranges are also contemplated. Temperatures below 280°F are also desireable.

Final T-90 temperature is function of improved latent heat of vaporization and/or improved combustion velocities, elicited by the reduction, which in turn is dependent upon the base fuel. Modifying differing fuels (and hydrocarbon

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streams) will elicit differing response. Thus, variability in actual amount of T-90 reduction is anticipated.

Example 125

5 A conventional or reformulated gasoline composition wherein higher boiling point fuel fraction is cut such that end point and/or T-90 boiling temperatures of the gasoline are reduced; and whereby the cut clear fuel's (e.g. reduced
10 t-90 fuel's) average latent heat of vaporization is at least 0.5% and more preferably 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 4.0%, 4.5%, 5.0%, 5.5%, 6.0%, 7.0%, 8.0%, 9.0%, 10%, 12.0%, 15.0%, 20.0%, 25.0%, 30.0%, or 2.0% to 50.0%, or greater, than the clear uncut fuel.

15 Example 126

 The composition of 125, additionally comprising sufficient quantity of a combustion chamber deposit control/modification additive or additive package (such as Texeco's CleanSystem³); and a minor amount of Mn; and
20 optionally an enhancing injector and/or intake valve deposit control additive; whereby adverse hydrocarbon emissions are controlled.

Example 127

25 The composition of 126, wherein after the inclusion of deposit control additive, or additive package, combustion temperatures are reduced.

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Example 128

The example of 125, wherein said adjusted and unadjusted T90 gasolines both comprise 1.0% to 2.0% oxygen by wt of MTBE and a cyclomatic manganese tricarbonyl having a Mn concentration from 0.001 to 0.03125 gr. mn/gal, such that fuel economy of the reduced boiling temperature fuel is improved over the unadjusted fuel.

Example 129

The example of 125, wherein T-90 temperatures of the adjusted reformulated fuel is approximately 260°F to 280°F, or less, and/or the driveability index is less than 1160, 1155.

It is also contemplated that toluene will constitute a greater compositional role, and exist in greater volume concentrations in future gasoline compositions, including aviation fuels. Contemplated toluene volume percent include 0.2, 0.5, 1.0, 2.0, 2.5, 3.0, 5.0, 5.5, 6.0, 7.0, 8.0, 10.0, 12.0, 15.0, 16.0, 18.0, 20.0, 25, 30.0, 35.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0 percentage.

Furthermore, limitation on Reid Vapor Pressures (RVP) are contemplated to for example equal to or less than 9.9, 9.5, 9.0, 8.7, 8.5, 8.2, 8.1, 8.0, 7.9, 7.7, 7.5, 7.0, 6.8, 6.5, 6.2, 6.0, 5.8, 5.6 PSI, or less. Limitations on sulphur concentrations are contemplated, including those less than 550, 500, 450, 400, 350, 300, 250, 200, 150, 100, 75, 50, 25, 20, 15, 10, 5 ppm, or less than 0.002 wt %,

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including sulfur free compositions, and naphtenes at less than 7% (or less than 0.5%, if practical) by volume are contemplated.

5 Emissions of paramount concern is toxic emissions, which this invention unexpectedly reduces, on a mass basis, on the order of 5%, or more, over conventional and other reformulated gasolines. This is a most unexpected development. For example, it has been found that the levels of 1,3-butadiene (a regulated toxic) increase in th
10 presence of MTBE when reducing olefins and T-90 temperatures. Furthermore, it has been found that formaldehyde exhaust emission actually increase when aromatics are reduced and/or when MTBE is added.

15 Example 130

An unleaded, phosphorus free, reformulated gasoline composition having a max of 8.5, 8.0, 7.5, 7.8, 7.7, 7.6, 7.5, 7.4, 7.4, 7.3, 7.2, 7.1, 7.0, 6.9, 6.8, 6.7, 6.6, 6.5, 6.4, 6.3, 6.2, 6.1, 6.0, 5.9, 5.8, 5.7, 5.6, 5.5, 5.4, 5.3, 5.2, 5.2, 5.0 psi RVP; a max of 5.0% to 10.0% vol olefins (6.0% to 9.0%, 6.0% to 10.0%, 5.0% to 8.0%), a max of 27, 25, 20, 19, 18% vol aromatics (preferably 15%, 10%, or lower), a max of 1.1, 1.0, 0.9, 0.8% benzene (preferably less than 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2% or benzene
25 free), a max of 100 ppm sulfur (preferably 50 ppm or less or sulfur free), an O2 concentration ranging from 1.8% to 2.2%, 2.0% to 2.7%, 3.5%, 3.7%, 4.0% O2 wt of dimethyl carbonate, MTBE, ETBE, TAME, ethyl tertiary amyl eth r,

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diisopropyl ether or ethanol, or mixture, a cyclomatic manganese tricarbonyl compound at 1/64 to 3/16 gr. Mn/gal (1/32 gr mn/gal preferred), a max T-90 temperature of 260°F to 280°F, or less, a T-50 temperature of approx. 160°F to 230°F (170°F to 205°F, 175°F to 210°F, 175°F to 225°F, 180°F to 210°F), maximum T-50 temperature equal to or less than 100, 110, 120, 130, 140, 145, 150, 155, 160, 170 degree F; a driveability index number equal to of less than 1200, 1190, 1180, 1170, 1160, 1155, 1150, 1140, a bromine number of not greater than 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, or less; an average latent heat of vaporization of 890, 900, 905, 910, 915, 920, 925, 930, 910 to 930, 915 to 940, 915 to 950, 920 to 960, 925 to 970, 930 to 980 BTU/gal, or greater.

15

Example 131

The Example of 130, wherein the fuel contains an ashless dispersant, induction control/deposit control additive (including combustion chamber, port fuel injector, and intake valve deposit additive) in conformity with § 211 (1) and appropriate regulations of the Clean Air Act; and optionally containing a minor amount of a co-solvent to enhance water solubility, such as hexanol.

25

Example 133

The Example of 130, 132, wherein the injected fuel particle has an approximate injected pressure of approximately 15 to 45 psi.

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Example 134

Method of combustion example 130, wherein the temperature of combustion is sufficiently reduced that under for example a load of 20 indicated horse power exhaust gas temperatures are reduced by at least 10°F to 50°F (or more), whereby the average exhaust gas temperature entering the exhaust gas inlet is less than 1400°F (or such other temperature that manganese oxide coating of the catalyst wash coat and/or monitor does not appreciably occur).

Example 135

A method for controlling the combustion formation of hazardous heavy manganese oxides comprising: Mixing an unleaded hydrocarbon fuel base, reformulated gasoline base, diesel base, or reformulated diesel (including those set forth herein) with a burning velocity increasing and/or combustion temperature reducing amount of an ECS compound, including one selected from the group consisting of carbonic acid dimethyl ester, methyl tertiary butyl ether, ethyl tertiary butyl ether, methylene di methyl ether, tertiary methyl amyl ether, diisopropyl ether, C1 to C6 alcohols, and mixture; and a combustion improving amount of at least one metallic compound, preferably a cyclomatic manganese tricarbonyl compound; combusting said fuel in an engine operating under load equal to or in excess of approximately 16.0 ihp; whereby combustion temperatures are reduced; exhausting engine out gas through an emission

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control system employing a reduction catalyst, particulate trap, or three way exhaust catalyst system; wherein said method avoids deposition of harmful heavy manganese oxides and/or other deposits upon combustion chamber, fuel injectors, or intake valves; emitting resultant exhaust into the atmosphere; whereby hazardous emissions are reduced.

Example 136

10 The method of Example 135, additionally comprising via the introduction of an ESC compound into said fuel, igniting said fuel, wherein H, H₂, OCH₃, or OH free radicals are formed in sufficient quantity as intermediate combustion product to increase said resultant fuel's
15 burning velocity over burning velocity of base fuel alone, absent ESC compound and/or metallic.

Example 137

20 The method of Example 135, wherein said engine is operated under a load of 20 ihp, or greater, whereby expected engine out combustion exhaust/gas temperatures or combustion temperatures are reduced by up to approximately 15°F to 59°F, or more, and/or where fuel economy is improved.

25 Example 138

The method of Example 137, wherein said resultant fuel has a combustion chamber deposit reducing/control additive

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and/or a mid-range and/or T-90/end-boiling distillation fraction temperature lower than existing conventional gasoline or diesel (or as otherwise set forth herein).

5 Example 139

A method, wherein reduced temperature engine exhaust gases are from an unleaded gasoline system and are vented through an exhaust emissions catalyst, whereby emission system's onboard catalyst monitoring does not fail due to
10 false catalyst oxygen storage capacity readings and/or oxide desposition upon the monitor.

Example 140

The above methods or compositions, wherein they can
15 qualify for an EPA waiver under § 211 (k) of the Clean Air Act.

Example 141

A low toxic fuel economy improving composition
20 comprising an unleaded fuel composition comprising phosphorus free hydrocarbons, having a max of 8.0, 7.0, 6.5, or 6.0 psi RVP; a max of 6.0%, 5.0% vol olefins, a max of 25%, 20% vol aromatics (preferably 15%, 10%, or lower), a max of 0.8% benzene (lower or benzene free) a max of 40
25 ppm sulfur (lower or sulfur free), a total O2 concentration ranging of 1.0 to 2.7% wt or 3.5% O2 wt of dimethyl carbonate, MTBE, ETBE, TAME, or ethanol, a cyclomatic manganese tricarbonyl compound at 1/64 to 3/16 gr. Mn/gal

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(preferably 1/32 gr. Mn), a max T-90 temperature of 300°F, 280°F (preferred), a T-50 temperature of approx. 170°F to 230°F., a minimum (R+M)/2 octane of 87, a bromine number of 20 or less, an average latent heat of vaporization of 900, 910, 920 or more BTU/gal at 60°F; a heating value greater than 106,000 btu/gal at 60°F (more preferably greater than 108,000, 114,000 btu/gal); whereby toxic 1,3-butadiene, formaldehyde, or acetaldehyde emissions are reduced and/or fuel economy is improved.

Example 142

The Example of 141, wherein the oxygenate is MTBE at 2.0% wt and the average latent heat of vaporization of the fuel exceeds 900 BTU/gal @ 60°F and is preferably greater than 905 BTU/gal @ 60°F; MMT concentration is 1/32 gr./gal; and average heating value of the composition exceeds 106,000 btu/gal at 60°F; has an average laminar burning velocity of at ambient conditions greater than 48 cm/sec.

Example 143

The MTBE composition of example 142, wherein the MMT concentration is greater than 1/32 gr mn/gal.

Example 144

The examples above, wherein the oxygenate is DMC and the MMT concentration is greater than 1/32 gr mn/gal.

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Example 145

The composition of examples 141, wherein RVP is 6.8, 6.5, 6.0, 5.5 psi or lower.

In the practice of this invention, in view of reducing regulated emissions, preferred gasoline compositions include, but are not limited to those which have the following specifications:

TABLE 6

LEAD FREE FUELS

	<u>A</u>	<u>B</u>	<u>C</u>
Reid Vapor Pressure (max psi)	8.7	.0	3.0-6.0
Olefin (max volume %)	9.2	8.0	.0-8.0
Aromatics (max volume %)	32.0	20.0-25.0	.0-10.0
Benzene (max volume %)	1.5	1.0	.0-0.5
Sulphur (max parts/million)	339	100	0.0-10
Oxygen (weight %)	0.0	2.0-2.7	2.0-5.0
T-90 (Max temperature °F)	330.0	320.0	300-330
(R & M)/2 (min)	87.0	87.0	87.0-95.0
DMC (optional) O2 wt	.8-2.1	2.0	2.7
LHV btu/lb	152	153	156
Burning velocity			
optional cm/sec (min)	49	51	50
Metallic (MMT)	1/64	1/32	1/30

25 Example 145a

A composition of matter comprising; an unleaded conventional or reformulated gasoline composition (the later conforming with § 211(k) of Clean Air Act), said

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composition additionally characterized as having a minimum latent heat of vaporization at 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156 btu/lb @ 60°F, and optionally a minimum laminar flame burning velocity of 45, 46, 47, 48, 49, 50, 51 cm/sec.

Example 146

The Example fuels of 145a, B and C of TABLE 6 above, wherein 1) said fuels contain Applicant's oxygenated means and a 2) combustion improving amount of manganese, and 3) wherein the combined evaporative emissions of said fuels' storage and its delivery to a combustion chamber, and emitted atmospheric combustion emissions, are 4) such that in the year 1995 said fuel's volatile organic compound emissions and toxic air pollutants, on a mass basis, are 15% lower than the baseline gasoline as defined under § 211 (k) of the Clean Air Act, and are 5) such that in the year 2000 said fuel's volatile organic compound emissions and toxic air pollutants, on a mass basis, are 25% lower than said baseline gasoline.

Example 147

An unleaded, phosphorus free, reformulated gasoline composition fuels having a max of 8.0, 7.2, 7.0, 6.5 psi RVP, a max of 8.0%, 6.0% vol olefins, a max of 20-25% vol aromatics, a max of 1%, 0.8% benzene (preferably less), a max of 300-40 ppm sulfur (preferably lower or sulphur free), an O2 concentration ranging from 2.0 to 2.7% wt or

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3.5% O₂ by weight of dimethyl carbonate, a cyclomatic manganese tricarbonyl compound or mixture at 1/64 to 3/16 gr. Mn/gal (preferably greater than 1/32 gr/gal), a max T-90 temperature of 300°F to 320°F (preferably 280°F or lower),
5 a preferred T-50 temperature of approx. 170°F to 220°F; a minimum latent heat of vaporization of 900, 905 BTU/gal @ 60°F (preferably greater than 920 BTU/gal @ 60°F); a minimum heating value of the composition assuming 2.0% O₂ weight of 106,000, 110,000, 113,000, 116,000 BTU/gal @ 60°F,
10 and a minimum average laminar burning velocity at ambient conditions of 48 cm/sec (50 to 52 cm/sec or more preferred).

Example 148

15 The above example wherein the composition additionally contains deposit control additives in conformity with § 211 (1) and related Sections/regulations of the Clean Air Act.

Example 149

20 Example 147, wherein the composition optionally contains at least one C₄ to C₆ alcohol or other additive assuring hygroscopic stability (water solubility).

Example 150

25 A fuel injection system that injects the fuel vapor of Example 19, under acceptable pressure into a combustion chamber, wherein average vapor particle sizes are less than 60 microns, and wherein computer enhanced EGR, an onboard

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oxygen sensor, injection sensors, air inlet cooling system or turbocharger is employed; whereby fuel synergism exists.

Applicant notes that said mechanical systems are synergistic to Applicant's invention in they show a greater incremental improvement for ECS fuels than clear co-fuels. Thus, the incremental improvement for ECS fuels divided by the incremental improvement for co-fuel (absent ECS component) is greater than one.

10 Example 151

A system, wherein the fuel injection system injects a fuel vapor under optimum pressure into a combustion chamber, wherein average vapor particle sizes are 10, 20, 30, or 40, wherein a turbocharger, EGR system, an onboard oxygen sensor, and injection sensors are simultaneously employed; whereby fuel economy is improved by at least 2%.

Example 152

A method, wherein the combustion chamber is designed to increase turbulent burning velocity, and wherein the compression ratio is 2.0:1 to 6.5:1; 7.5:1, 8.0:1, 8.5:1; 9.0:1; 9.5:1, 10:1, 10.5:1, 11.0:1, and more preferable 11.5:1.

25 Example 153 [Omitted]

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Example 154

The above examples, wherein the compression ratio ranges from 9.5:1 to 12.5:1.

5 Example 155

The examples above, wherein the combustion chamber is designed to increase turbulent burning velocity, and wherein the compression ratio exceeds 17:1.

10 Example 156

The examples above, wherein the combustion system operates in conjunction with a regulated exhaust/emission control system employing an emission catalyst and an on-board oxygen sensor.

15

Example 157

A method of operation, wherein at least 30% of the U.S. automotive fleet operates on said fuels, whereby total reference concentrations of air borne manganese emitted from such operation, does not exceed 0.05 ug/m³ or EPA standards, which ever is lower.

20

Applicant's gasoline compositions expressly contemplate reductions in emissions and compositional characteristics as set forth in Tables 7 and 8, below.

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TABLE 7

COMPLEX MODEL STANDARDS FOR RFG

	PROPERTIES	PHASE 1	PHASE 2
		1995	2000 and after
5	VOC REDUCTION (%) / GAL(1)		
	Class B	35.1	27.5
	Class C	15.6	25.9
10	NOx REDUCTION (%) (1)		
	Summer	0-1.5	5.5-6.8
	Winter	0-1.5	0-1.5
15	TOXICS REDUCTION(1)	15.0-16.5	20.0-21.5
	OXYGEN (WT%)	2.0-2.1	2.0-2.1
20	BENZENE (vol%)	0.0-1.0	0.0-1.0
25	Note 1	Reductions are from the baseline gasoline defined under § 211 (k) (10) (B)	

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TABLE 8**EXAMPLE FUELS COMPLYING WITH CLASS C RFG REGULATIONS**

5	PROPERTIES	PHASE 1 1995-2000	PHASE 2 2000 and After
	REDUCTION % (1)		
10	VOC'S	17.3	27.6
	NOX	1.6	6.9
	TOXICS	25.4	27.6
15	PROPERTIES		
	RVP (psi)	8.0	6.6
	OXYGEN (WT%) (2)	2.1	2.1
	AROMATICS (VOL%)	25.0	24.0
20	BENZENE (VOL%)	0.95	0.95
	OLEFINS (VOL %)	9.2	9.2
	SULPHUR (ppm)	339	185
	E200	41.0	45.0
	E300	83.0	87.0
25	Manganese (Gr. Mn/g) (3)	1/32	1/32
30	Note 1	Reductions are from the baseline gasoline defined under § 211 (k) (10) (B)	
	Note 2	In the form of dimethyl carbonate.	
35	Note 3	Manganese concentrations may range from 1/64 to 1/4 gr. Mn/gal.	
40	An example of a reformulated gasoline comprises a gasoline base with less than 0.01% wt sulfur, MTBE 7% max. by vol., benzene 5.0% or less by vol., kerosene 4.0% or less by vol., existent gum 5 mg/100 ml max, unwashed gum 20 mg/100 ml max, RON 96.0 to 89.0, density at 15°C 0.783 max,		
45	T10 70°C max, T50 125°C max, T90 180°C max, F.B.P. 220°C max, Residue 2% max, copper corr. max 1, RVP 44-78 kPa, induction time min. of 240 min		

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In the practice of this invention, when formulating gasoline compositions to meet RFG standards, tailoring may be required to accomplish the objects of this invention. It has been found that various components, which have the largest effect in reducing specific target emissions may be tailored: For example, VOC's are effected mostly by RVP, Aromatics, Sulphur. NOx are effected mostly by Sulphur, Aromatics, Olefins; and Toxics are effected mostly by Benzene, Aromatics, oxygen.

10 International Application No. PCT/US95/02691 presents reformulation practice, which is incorporated by reference.

Reductions in sulfur content linearly influence reductions in NOx, toxic, and VOC emissions (in order of their relative % emission reductions). For example, a reduction in sulfur from 340 ppm to approximately 50 ppm causes a reduction of NOx, toxic, and VOC emissions of about 11.0%, 8.5%, and 3.5%, respectively. It appears that reductions in NOx emissions are strongly influenced by reductions in sulfur content. In the practice of this invention sulfur concentrations less than 40 ppm are particularly preferred. Sulfur content 30 ppm or less (or sulphur free) is even more preferred. Again, the operation of this invention will permit environmentally acceptable NOx, Toxics, and VOC's even at sulfur concentrations higher than currently permitted under the regulations.

25 However, sulfur concentrations on the order of 200 ppm or more appear to be acceptable, due the increased burning velocity and reduced combustion temperatures of instant

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invention, which appear to inhibit sulfur's adverse NOx and Toxic emission characteristics.

Aviation Gasoline

5 The invention also contemplates aviation gasoline co-fuel applications and resultant fuels meeting ASTM D 910 specifications (see TABLE 9), especially those that are lead free. However, unlike other embodiments of Applicant's invention, while less preferred aviation gasolines may
10 contain minor amounts of lead. However, Applicant's preferred embodiment is lead free.

 Applicant's invention contemplates a broad application in aviation gasolines for civil and military use, including those applications, which do not comply with ASTM
15 standards. Thus, TABLE 9 is intended to define aviation gasoline suitable for most types of spark-ignition aviation engines; however, certain equipment or conditions of use may require fuels having other characteristics.

 A major problem with aviation gasolines and related
20 combustion resides in the substantial incompleteness of combustion at altitude. Combustion incompleteness is a function of the fuel's composition, air/fuel ratio's, altitude of operation, and generally the amount of air passing through the engine.

25 The principal advantage of Applicant's invention is that it radically improves the thermal efficiency or useful amount of work available from a given amount of fuel under operation at altitude, compared to traditional fuels.

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In today's aviation gasoline engines the completeness of combustion under altitude conditions approaches 85% (see M. Scott, R Stansfield, T. Tait, J. Inst. Petroleum. 37, 487 (1951)).

5 Quite unexpectedly, in the practice of Applicant's invention completeness of combustion and thermal efficiency at altitude increases over 2.0%, 5.0%, 7.5%, 10.0%, or more. Thus, the flight range of an aviation gasoline powered aircraft employing Applicant's composition and
10 method should be extended 2%, 3%, 4%, 5% to 30%, or more, depending upon application.

Example 158

 A aviation fuel boiling meeting ASTM specifications
15 comprising: an ESC fuel (containing preferably MMT at 0.25 to .75 Mn gr/gal of finished fuel and DMC ranging from 0.5% to 10.0% of finished fuel), a aviation co-fuel comprised substantially of hydrocarbons; such that resultant fuel meets strict ASTM standards; and is characterized as having
20 a latent heat of vaporization exceeding 120, 130, 140, 150, 155, 160, 165, 170 BTU/lb; and whereby said fuel when combusted in an internal combustion engine at altitude of at least 5,000 feet above ground level increases the completeness of combustion to amount greater than 85%, 86%,
25 87%, 88%, 89%, 90%, or alternatively increases thermal engine efficiency by at least 2.0%, 3.0%, 5.0%, 7.5%, 10.0%, or more, over the unadjusted aviation co-fuel.

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TABLE 9

ASTM D 910

AVIATION GASOLINES^v

5

	Grade 80	Grade 100	Grade 100LL	ASTM Test Method ^B
10				
Knock value, min, octane number, lean rating	80	100	100	D 2700 ^C
Knock value, min, rich rating:				
Minimum octane number	87			D 909
15 Minimum performance number ^{O,P}		130	130	D 909
Color ^D	red ^E	green	blue	D 2392
Dye content:				
Permissible blue dye, ^F max, mg/gal	0.5	4.7	5.7	
Permissible yellow dye, ^G max, mg/gal	none	5.9	none	
20 Permissible red dye, ^H max, mg/gal	8.65	none	none	
Tetraethyllead, ^I max, mL/gal	0.5 ^E	4.0	2.0	D 2559 or D 3341
Requirements for all Grades				
25 Distillation temperature, °F (°C):				
10 % evaporated, max temp	167 (75)			D 86
40 % evaporated, min temp	167 (75)			
50 % evaporated, max temp	221 (105)			
90 % evaporated, max temp	275 (135)			
30 Final boiling point, max, °F (°C)	338 (170)			
Sum* of 10 and 50 % evaporated temperatures, min, °F (°C)	307 (135)*			
Distillation recovery, min, %	97			
Distillation residue, max, %	1.5			
35 Distillation loss, max, %	1.5			
Net heat of combustion, ^J min, Btu/lb	18 720			D 1405 or D 3338
Vapor pressure:				
min, psi (kPa)	5.5 (38)			D 323 or D 2551
max, psi (kPa)	7.0 (49)			D 323 or D 2551
40 Copper strip corrosion, max	No. 1			D 130
Potential gum (5-h aging gum), ^K max, mg/100 mL	6			D 873
Visible lead precipitate, ^L max, mg/100 mL	3			D 873
Sulfur, wt max, %	0.05			D 1266 or D 2622
Freezing point, max, °F (°C)	-72 (-58)			D 2386
45 Water reaction	volume change not to exceed ± 2 mL			D 1094
Permissible antioxidants, ^M max, lb/1000 bbl (42 gal)	4.2			

50 ^A Requirements contained herein are absolute and are not subject to correction for tolerance of the test methods. If multiple determinations are made, average results shall be used.

^B The test methods indicated in this table are referred to in Section 9.

^C The values shown in Table 1 represent Aviation Method Ratings. Motor octane ratings obtained by Test Method D 2700 should be converted to aviation ratings by Conversion Table 2.

55 ^D These colors have been approved by the Medical Director Chief, Division of Occupational Health, U.S. Department of Health, Education and Welfare.

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TABLE 9
(continued)

60

ASTM D 910

AVIATION GASOLINES^N

65 ^E If mutually agreed upon between the purchaser and the supplier, Grade 80 may be required to be free from tetraethyllead. In such a case, the fuel shall not contain any dye and the color as determined in accordance with Test Method D 156 shall not be darker than +20.

^F The only blue dye which shall be present in the finished gasoline shall be essentially 1,4-dialkylamino-anthraquinone.

70 ^G The only yellow dyes which shall be present in the finished gasoline shall be essentially p-diethylaminoazobenzene (Color Index No. 11021) or phenol, 2,2'-[3,3'-dimethyl][1,1'-biphenyl]-4,4'-diyl]bis(azo) bis [4-nonyl] (Color Index Solvent Yellow No. 107), or 1,3-Benzenediol, 2,4-bis [(alkylphenyl)azo-].

75 ^H The only red dyes which shall be present in the finished gasoline shall be essentially methyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105) or alkyl derivatives of azobenzene-4-azo-2-naphthol.

80 ^I The tetraethyllead shall be added in the form of an antiknock mixture containing not less than 61 weight % of tetraethyllead and sufficient ethylene dibromide to provide two bromine atoms per atom of lead. The balance shall contain no added ingredients other than kerosine, and an approved inhibitor, and blue dye, as specified, herein.

^J Use the value calculated from Table 1 in Test Method D 1405. Test Method D 2382 may be used as an alternative method. In case of dispute, Test Method D 2382 must be used. In this latter case, the minimum values for the net heat of combustion in Btu's per pound shall be 18 700 for Grades 80, 100, and 100LL.

85 ^{*} Note that the temperature conversion for the sum is $C_1 + C_2 = 5/9 (F_1 - 32 + F_2 - 32)$.

^K If mutually agreed upon between the purchaser and the supplier, aviation gasoline may be required to meet at 16-h aging gum test (Test method D 873) instead of the 5-h aging gum test. In such a case, the gum content shall not exceed 10 mg per 100 ml and the visible lead precipitate shall not exceed 4 mg per 100 mL. In such fuel the permissible antioxidants shall not exceed 8.4 lb per 1000 bbl (42 gal).

90 ^L The visible lead precipitate requirement applies only to leaded fuels.

^M Permissible antioxidants are as follows:

N,N'-diisopropyl-para-phenylenediamine

N,N'-di-secondary-butyl-para-phenylenediamine

95 2,4-dimethyl-6-tertiary-butylphenol

2,6-ditertiary butyl-4-methylphenol

2,6-ditertiary butylphenol

75% min 2,6-ditertiary butylphenol plus 25% max tertiary and tritertiary butylphenols

75% min di- and tri-isopropyl phenols plus 25% max di- and tri-tertiarybutyl phenols

100 These inhibitors may be added to the gasoline separately or in combination, in total concentration not to exceed 4.2 lb of inhibitor (not including weight of solvent) per 1000 bbl (42 gal).

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Three principal grades of aviation gasoline contemplated by this invention, which meet ASTM standards, include: Grade 80, Grade 100 and Grade 100LL.

5 Grades 100 and 100LL represent two aviation gasolines identical in anti-knock quality but differing in maximum lead content and color. The color identifies the difference for engines that have a low tolerance to lead.

10 Although the grade designations show only a single octane rating for each grade, each grade must meet a minimum lean mixture aviation rating and a minimum rich mixture super-charge rating.

15 Aviation gasoline has traditionally been comprised of substantial quantities of isooctane and/or alkylated material. Applicant contemplates his aviation gasoline co-fuels may consist of blends of refined hydrocarbons derived from crude petroleum, natural gasoline, alkylates, blends thereof from synthetic hydrocarbons or aromatic hydrocarbons, or both. Aviation gasolines has may derived in whole or part from bio-substituents.

20 As thermal efficiency improvements are a principal object of this invention, aside from constructing fuels to acheive the maximum latent heats of vaporization and to meet strict ASTM standards (including heat of combustion, etc.), Applicant's preferred order of fuel components (in
25 order of their preference) are: paraffins, monocyclic naphthenes, cyclo-olefins, bicyclic naphenes, aromatic monocyclic with side chains, aromatic monocyclics and aromatic bicylics.

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Applicant has found that by prioritizing his fuel components, after meeting his LHV object and ASTM standards, that Applicant is further able to improve thermal efficiency.

5 Additional aviation gasoline practice is disclosed in International Application No. PCT/US95/02691 and incorporated by reference.

Additives other than tetraethyl lead, dyes, and antioxidants specified in Table 9 are permitted under 5.1
10 and Section 7 of ASTM specification D 910. These include fuel system icing inhibitor and special purpose additives.

Additional aviation gasoline practice is disclosed in International Application No. PCT/US95/02691 and incorporated by reference.

15 In Applicant's preferred practice DMC is employed as the ECS compound of choice. Due to the high relative concentrations of oxygen (e.g. 53% by weight), smaller volume quantities of DMC need be employed to achieve the same oxygen concentrations as MTBE (e.g. 18.2% by wt), TAME
20 (e.g. 15.7% by wt).

Thus, on a heat of combustion basis, while DMC has lower total heat per gallon (e.g. approx. 57,000 btu/gal) compared to MTBE's (e.g. approx 94,200 btu/gal), TAME (100,600 btu/gal), DMC has superior heat of combustion on
25 a per oxygen weight basis. Consequently, a co-fuel can maintain a greater proportion of its heat of combustion, given the same amount of oxygen, when said oxygen is added by DMC as compared MTBE, ETBE or TAME. Thus, the addition

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of DMC reduces the amount of additional high heating material necessary to achieve minimum heats of combustion.

Example 159

5 A method wherein a enhanced combustion vapor is combusted in a aviation gasoline engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel (more preferably 0.1 to 5.0%), at least one metallic in a concentration of 0.001 to about 2.5 gr/gal (preferably
10 0.001 to 1.5 gr/gal, more preferably 0.001 to 0.75), an aviation gasoline co-fuel; wherein combined fuel is characterised as having a minimum knock octane number of 80, or 100 and minimum performance number of 87, or 130, optionally containing lead, a max T10 distillation
15 temperature of 75°C, a minimum T40 temperture of 75°C, a maximum T50 temperature of 105°C, a maximum T90 temperature of 135°C, a maximum end temperature of 135°C, where the sum of the T10 and T50 temperatures is a minimum of 135°C, a maximum sulfur content of 0.05 wt%, optionally a minimum
20 net heat of combustion of 17,500, 18,000, 18,500, 18,720, 19,000, 19,500 BTU/lb, a latent heat of vaporization exceeding 125, 130, 135, 140, 145, 150, 155, or 160 BTU/lb; whereby when combusted in said aviation engine at altitude of at least 5,000, 10,000, 15,000 feet above ground level
25 combustion completeness or thermal efficiency (as reflected in range) is greater than unadjusted aviation co-fuel alone (preferably at least 2.0% or more).

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Example 160

A method of operating a gasoline aviation engine on an enhanced combustion vapor, wherein said vapor is combusted in an aviation gasoline engine; and is derived from an ECS compound representing 0.01% to 15.0% oxygen by weight of a fuel, an organo manganese representing about 0.001 to 3.0 gr Mn/gal of fuel, and an ASTM or other aviation co-fuel having a minimum heat of combustion of 18,720 BTU/lb; whereby said combined fuel has heat of combustion lower than 18,720 BTU/lb due to dilution effect of DMC; said method characterized in that aviation engine combusting lower heat of combustion vapor has increased flight range compared to higher heat of combustion vapors from co-fuel alone (preferably greater than 2.0%).

15

Example 161

A method above, wherein said engine is operated on an air-fuel ratio of 30, 35, 40, 45, 50, 55, 60 (preferably 35 to 60, more preferably 40 to 60; wherein said operation employing DMC represents an incremental thermal efficiency improvement for ECS fuel over same improvement, if any, for co-fuel alone.

20

Example 162

An unleaded aviation fuel composition meeting ASTM standards comprising 2.0% oxygen by weight in form of an ECS compound (preferably DMC), a combustion enhancing amount of a metallic (preferably manganese in a

25

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concentration of 1/4 to 5/8 gr/gal), and a minimum heat of combustion of 18,720 BTU/lb; whereby the incremental lost heat of combustion of the composition due to addition of ECS compound is less 1500, 1000, 750, 500, 300 BTU/gal or 250, 160, 120, 80, or 50 btu/lb.

Example 163

A liquid aviation gasoline fuel comprising DMC at 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5%, or more, oxygen by weight in the fuel and at least one manganese metallic representing 0.001 to 1.5 gr/gal, and an aviation co-fuel base; wherein combined fuel is characterised as having a minimum knock octane number of 80, 100, 100, and minimum performance number of 87, 130, 130, a max T10 distillation temperature of 75°C, a minimum T40 temperture of 75°C, a maximum T50 temperature of 105°C, a maximum T90 temperature of 135°C, a maximum end temperature of 135°C, where the sum of the T10 and T50 temperatures is a minimum of 135°C, a maximum sulfur content of 0.05 wt%, a minimum net heat of combustion of 18,720 BTU/lb, a latent heat of vaporization exceeding 120, 130, 140, 150, 155, or 160 BTU/lb.

Example 164

The example of 162, wherein fuel originally meets ASTM D 910 heat of combustion standards; and wherein 2.0% oxygen by weight in form of DMC is added, together with manganese in a concentration from about 1/4 to 5/8 gr/gal; said

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resultant composition is not adjusted for loss of heat due to addition of DMC; operating said aviation engine on lower heat of combustion fuel, whereby flight range is increased by at least 2.0% greater over original ASTM clear aviation co-fuel.

Example 165

An ASTM aviation gasoline comprising a hydrocarbon base, a minimum octane or performance number of 87 or 130 (ASTM 909), a distillation fraction wherein the sum of the T-10 plus T-50 fractions are 307°F, the T-40 temperature is 167° F and the T-90 temperature is less than 250°F, with the fuel sulfur content a maximum of 0.05 wt% (preferably less), and a combustion improving amount of an ECS compound; whereby the resultant fuel's latent heat of vaporization exceeds 120, 125, 130, 135, 140, 142, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 152, 153, 154, 155, 156, 157, 158, 159, 160, 162, 165 BTU/lb; and whereby resultant fuel optionally has a laminar burning velocity equal to or exceeding 40, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52 cm/sec.

Example 166

The example of 165, wherein the aviation gasoline composition is unleaded and comprises a blend of hydrocarbons, a combustion improving amount of CMT ranging from 0.001 to 3.00 gr. Mn/gal, more preferably 0.001 to 2.0 gr. Mn/gal, 0.001 to 0.1 gr. mn/gal, 0.001 to 0.8 gr

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mn/gal, 0.001 to 0.6 gr mn/gal, 0.125 to 0.5 gr mn/gal
(minimum amounts greater than 1/4, 3/8 gram/gal preferred),
a combustion improving amount of DMC ranging from 0.01% to
20.0% O₂ by weight (1.5% to 5.0% preferred, 1.5% to 2.5%
5 more preferred), whereby the octane rating number as
determined by ASTM D 2700 is at least 100, with the balance
of the fuel's specifications strictly conforming to strict
ASTM standards; and whereby the fuel's LHV exceeds 145,
144, 145, 146, 147, 148, 149, 150, 152, 153, 154 BTU/lb.

10

Example 167

The unleaded composition of 165, wherein CMT is
greater than 1/16, 1/8, 1/4, 1/2, or 5/8 gram Mn/gal, and
the combustion improving amount of DMC is greater than 1.0%
15 O₂ by weight, preferably greater than 1.5%, and the minimum
net heat of combustion of composition is approximately
18,500 BTU/lb, 18,720, 18,800 BTU/lb., or more preferably
greater than 19,000 BTU/lb, and flight range is increased
over clear fuel alone.

20

Example 168

The unleaded composition of 165, wherein CMT is
greater than 1/16, 1/8, 1/4, 1/2, or 5/8 gram Mn/gal, and
the combustion improving amount of DMC is greater than 1.0%
25 O₂ by weight, preferably greater than 1.5%, and the net
heat of combustion is approximately 16,500 to 18,500
BTU/lb, wherein flight range is increased at least 5% over
the clear fuel.

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Example 169

A method of operating a aviation gasoline power aircraft; said method characterized: by mixing a fuel of example 165, supplying said fuel to an injection or vaporization system, wherein said fuel is injected into an engine manifold or combustion chamber, wherein average fuel droplet particles is less than 80, 70, 60, 50 microns; whereby combustion of said fuel results in an increase in power, thermal or combustion efficiency greater than clear fuel preferably 2.0% or more.

Example 170

A method above, wherein the fuel is constructed employing DMC such that combustion temperatures are reduced by at least 25°F, and whereby thermal efficiency is improved by 5% to 10% and/or the operation of aviation gasoline engine life is extended by at least 5.0%

Example 171

The example of 169-170, wherein the fuel additionally has an end boiling temperature of less than 300°F, (or alternatively a T-90 temperature less than 250°F), and an average latent heat of vaporization increased over base fuel by at least 2.0%, preferably 5.0%, or more.

25

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Example 172

The examples above, wherein the fuel's aromatic content is less than 20 volume percent, and wherein benzene is less than 1.0% by volume.

5

Example 173

The examples of 169-170, wherein the fuel is combusted in a spark ignited internal combustion engine, equipped with fuel injection or manifold, and/or other means, wherein fuel particles averaging 70, 60 microns, or less, are communicated/injected into the combustion chamber; and wherein said combustion is occurring at an altitude of at 5,000 to 10,000 feet above sea level, or more; and wherein combustion efficiency is increased by at least 5.0%.

10
15Example 174

The aviation gasolines of the above examples meeting ASTM D 910 specifications, and a combustion improving amount of dimethyl carbonate and CMT in a concentration from about 0.001 grams to about 0.125 grs per gallon.

20

Example 175

In combination, an aviation gasoline meeting ASTM D 910 specifications, a spark ignited aviation gasoline engine, wherein said combination is characterized in that: said fuel contains a combustion improving amount of dimethyl carbonate up to 5.0% oxygen wt/gal, and a least one CMT compound in a concentration from about 0.001 grams

25

TABLE 10
(continued)
ASTM D 396

DETAILED REQUIREMENTS FOR FUEL OILS^A

Property	ASTM Test Method ^B	No. 1	No. 2	Grade No. 4 (Light)	No. 4	No. 5 (Light)	No. (Heavy)	No. 6
Density at 15°C, kg/m ³	D 1298	>876 ^F
min	
max		850	876
Pour Point °C, max ^G	D 97	-18	-6	-6	-6	^H

^A It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller and manufacturer.

^B The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

^C The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 mass %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

^D Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

^E Other sulfur limits may apply in selected areas in the United States and in other countries.

^F This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

^G Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than -18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm²/s and the minimum 90 % recovered temperature shall be waived.

^H Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as Low Pour (+15°C max) or High Pour (no max). Low Pour fuel oil should be used unless tanks and lines are heated.

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There is generally no limit on T-10 or T-50 reductions, nor T-90 reduction (except for No. 2 fuels) so long as the fuel is easily vaporized and operates efficiently, particularly in vaporizing type burners.

5 A minimum T-90 temperature limitation for Grade No. 2 heating oil is intended to maintain compatibility with atomizing type household heating burner applications. Otherwise, distillation limits are not specified for fuel oils of Grade Nos. 4, 5, and 6, and T-90 temperatures may
10 be reduced to the extent practical, in order to improve combustion and/or reduce pollutants.

Example 176

15 A No. 2 fuel oil, with a kinetic velocity of no less than 1.9 nor greater than 3.4 (mm^2/s) measured at 40°C, a minimum T-90 temperature of 282°C, a max T-90 temperature of 338°C, a maximum sulfur content of 0.05% mass, a maximum copper strip rating of No.3, a combustion improving amount of an ECS compound (preferably DMC); and optional metallic,
20 flash point of 38°C, LHV of at least 90, 95, 100, 105, 110, 115, 120, 125, 130, 135 BTU/lb; said fuel optionally containing co-solvent and/or metallic salt.

Example 177

25 A No. 6 fuel oil, with a kinetic velocity of no less than 15.0 nor greater than 50.0 (mm^3/s) measured at 100°C using ASTM D 445, and combustion improving amount of an ECS compound, optionally a metallic.

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to about 1.00 grs Mn/per gallon, wherein said fuel comports to ASTM requirements; and whereby improved engine thermal efficiency is 2.0%, or more.

5 **Fuel Oils**

The invention contemplates the use of a wide spectrum of fuel oils, as co-fuels, including burner fuels, fuel oils, furnace oils, petroleum and petroleum oils, and those fuel oils meeting ASTM D 396 standards, and/or fuel
10 intended for use in various types of fuel-oil-burning equipment, under various climatic and operating conditions. Non-limiting examples, include ASTM Grades 1 through 5, which are found at TABLE 10.

International Application No. PCT/US95/02691 sets
15 forth in detail Applicant's Fuel oil practice, which is incorporated herein by reference.

As noted, boiling point modification of fuels oils is an express embodiment of this invention, especially that resulting increased LHV's. It is expressly contemplated
20 that T-90 temperatures herein be reduced to maximum extend practical, but not below minimum required specification temperatures. For example, T-90 temperatures may be reduced 20° C below max ASTM specification temperatures. Reductions of 50° C are also preferred so long as, as in the case of
25 Grade No. 2 fuel oils, T-90 is not reduced below 282° C.

TABLE 10
ASTM D 396
DETAILED REQUIREMENTS FOR FUEL OILS⁴

Property	ASTM Test Method ^B	No. 1	No. 2	Grade No. 4 (Light)	No. 4	No. 5 (Light)	No. (Heavy)	No. 6
Flash Point °C, min.	D 93	38	38	38	55	55	55	60
Water and sediment, % vol. max	D 1796	0.05	0.05	(0.50) ^c	(0.50) ^c	(1.00) ^c	(1.00) ^c	(2.00) ^c
Distillation temperature °C	D 86							
10 % vol recovered, max		215
90 % vol recovered, min		...	282
max		288	338
Kinematic viscosity at 40°C, mm ² /s	D 445							
min		1.3	1.9	1.9	>5.5
max		2.1	3.4	5.5	24.0 ^p
Kinematic viscosity at 100°C, mm ² /s								
min		5.0	9.0	15.0
max		8.9 ^p	14.9 ^p	50.0 ^p
Ramsbottom carbon residue on 10% distillation residue % mass, max	D 524	0.15	0.35
Ash, % mass, max	D 482	0.05	0.10	0.15	0.15	...
Sulfur, % mass max ^E	D 129	0.50	0.50
Copper strip corrosion rating, max, 3 h at 50°C	D 130	No. 3	No. 3

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Example 178

The example of 176-177, wherein end boiling point and/or T-90 fraction temperatures are reduced at least 30°C, employing boiling point modification; whereby LHV are improved.

Example 179

The operation of burners in a furnace, employing an ASTM grade fuel oil, containing a combustion improving amount of dimethyl carbonate and a combustion improving metallic, wherein expected combustion efficiency of the furnace increases in range of at least 1.0% to 20%.

It is contemplated in locomotive and marine fuels meeting appropriate ISO DIS 8217 and BS MA 100 standards, containing higher concentrations of sulfur than most fuels, Applicants invention due combustion temperature object, mitigates sulfur corrosion and generation of other pollutants.

20

Example 180

A method for enhanced combustion of a vapor for heavy diesel, locomotive or marine engine; wherein vapor is derived from DMC representing 0.01% to 40% oxygen by wt in the fuel, a metallic representing 0.01 to 20.0 grs of metal/gal, and a heavy diesel, locomotive or marine engine co-fuel meeting ISO DIS 8217 and/or BS MA 100 standards specifications; wherein said combination contains a sulfur

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concentration of 0.01 to 3.0% mass, has a viscosity of 10 to 500 centistokes at 50°C; whereby combustion of said vapors results in reduced corrosion, particulate emissions and/or improved fuel consumption compared to co-fuel alone.

5

Example 181

The method of 180, wherein said operation of said heavy diesel, locomotive or marine engine is under load (moderate to high load conditions); whereby fuel consumption is improved by at least 0.5% to 5.0%, or more, over fuel absent ECS fuel.

10

Example 182

The fuel composition of example 180, additionally contains an ashless dispersant, which may be selected from an alkenyl succinic acid esters, alkenyl succinimide of an amine, methylamine, 2-ethylhexylamine, n-dodecylamine, and the like (see U.S. Patents 3,172,892; 3,202,678, 3,219,666, 4,234,435) and/or a combustion chamber deposition control additive.

15

20

Example 183

The fuel composition of example 180-181, wherein the ECS fuel contains dimethyl carbonate from 0.01 to about 30.0% volume and a combustion improving amount of CMT.

25

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Example 184

A method of improving thermal efficiency in the operation of a locomotive or marine engine, wherein said method comprises: injecting an ECS based heavy fuel composition into a combustion chamber, wherein combustion occurs at an accelerated, more efficient rate, and combustion temperatures are reduced; whereby thermal efficiency increased by at least 5%.

10 ADDITIVE PRACTICE

As set forth herein additive practice is a vital component of this invention. It is expressly contemplated that additives, additive methods, lubricants, and the like, set forth above in the various co-fuel applications be
15 interchangeable between co-fuels and neat fuel applications.

It is an express object of this invention to maximize the durability of fuel system components, prevent intake valve sticking, minimize combustion chamber deposits and the like.

20 Appliant's invention contemplates a wide range of additives and concentrations, including but not limited to the following (with approximate additive concentration): anti-oxidant(s) (8-40 mg/kg), wax anti-setting (100-200 mg/kg), anti-foam (2-5 mg/kg), anti-valve seat recession
25 (100-200 mg/kg), pipe-line drag reducing agents (2-20 mg/kg), diesel detergents (10-300 mg/kg), demulsifiers (3-12 mg/kg), diesel flow improvers (50-1000 mg/kg), deposit control additives (50-3000 mg/kg), lubricity improvers (25-

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1000 mg/kg), anti-static (2-20 mg/kg), stabilizers (50- 200 mg/kg), anti-icing agents (0.1-2.0% vol), corrosion inhibitor (4-50 mg/kg), combustion chamber deposit modifiers (50-3000 mg/kg), metal deactivator (4-12 mg/kg),
5 dyes (2-20 mg/kg), cetane/octane improvers (200-2000 mg/kg). Other contemplated additives include combustion improvers, biocides, drag reducing agents, dehazers, metallic scavengers, friction modifiers, antiwear additives, antisludge additive.

10 Non-limiting examples of Applicant's anti-static additives include soluble chromium materials, polymeric sulfur, nitrogen compounds, and quaternary ammonium materials. Use is generally contemplated in very cold ambient temperatures and/or in fuels of intermediat
15 volatility such as aviation kerosenes.

Non-limiting examples of metal deactivators include N,N'-disalicylidene -1, 2 - propanediamine, and its basic mechanism is to chelate dissolved copper, mitigating surface formation of metallic salts/deposits, etc. Non-
20 limiting examples of drag reducing agents include high molecular weight (1,000,000) polyisobutenes and polyalphaolefins.

Non-limiting examples of dyes include azo compounds and/or anthraquinone. Non-limiting examples of
25 demulsifiers include complex non-ionic surfactants, alkoxylated polyglycols and aryl sulfonates, and mixture (typically at treat rates in the range of 10-20% of that of the detergent, if any). Non-limiting examples of corrosion

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inhibitors include carboxylic acid, amines, and/or amine salts of carboxylic acids are used. Mobile Chemical Corp. markets "Mobiladd F-800" a combination lubricity agent and corrosion inhibitor. Non-limiting examples of anti-oxidants
5 include hindered phenols, phenylenedimines, aromatic diamines, or mixtures of aromatic diamines and alkyl phenols,. Disperants could be ashless succinimides or polymeric methacrylates,

Non-limiting examples of anti-icing additives include
10 isopropyl alcohol, hexylene glycol, dipropylene glycol, glycols, formamides, imidazolines and carboxylic acids. Non-limiting examples of valve seat recession additives include sodium or potassium long chain alkenyl sulfonates, sodium or potassium long chain naphthenates, or
15 microdispersions of sodium or potassium salts in oil.

Applicant's invention contemplates carburetor, port fuel injector and intake valve deposit control additives. Non-limiting examples include amides, amines, amine carboxylates, alkenyl succinimides, polybutene succinimides,
20 polyalkenyl succinimide (Ethyl Petroleum Additives, Inc., HITEC 4450), polyether amines, polyether amide amines, polyalkenyl amines, polyether amines (Oronite Chemical Co. OGA-480), polyisobutenyl amine (Oronite Chemical Co. OGA-472), polybuteneanines, polyetheramines, and polyolefin
25 amines, with or without carrier fluid. Such materials may be incorporated at treat concentrations of 50 to 500 pounds per thousand barrels, and more usally in the range of 100 to 200 lbs per thousand barrels. Other examples include

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Additional detergent/dispersants, include high molecular weight polyisobutylene substituted amine derivative TFA-4681, fuel soluble salts, amides, imides, oxazolines and esters of long aliphatic hydrocarbon-substituted dicarboxylic acids or their anhydrides, long chain aliphatic hydrocarbons having a polyamine attached directly thereto, a Mannich condensation product(s) formed by condensing a long chain aliphatic hydrocarbon-substituted phenol with an aldehyde, preferably formaldehyde, or similar additive is contemplated in the practice of keeping fuel injectors and valve intakes clean.

As noted, it is an express embodiment to employ combustion chamber deposit additives (except where deleterious to enhanced combustion feature of invention), especially those that reduce existing combustion chamber deposits. It is contemplated that certain deposit additives, which control injector and valve intake deposits, may be deleterious to combustion chamber deposition control or reduction and are therefore not as desirable.

Smoke suppressants, including organic compounds of barium, particularly the barium carbonate overbased barium sulfonates, N-sulfinyl anilines, are contemplated, as well as others.

Additional deposit control additives include, a polyether amine sold by Oronite Chemical as OGA-480, a polyalkenyl succinimide sold by Ethyl Corp as HITEC 4450,

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a polyisobutenyl amine sold by Oronite Chemical as OGA-472, and the like.

Example diesel fuel additives are shown by class and function in Table 4. As with any system in which a variety
5 of additives may be used, care should be taken to avoid incompatibilities among additives and unanticipated interactions which may produce undesirable fuel effects.

It is contemplated the fuel will contain other deposit control additives, non-limiting examples include polyether
10 amine, polyalkenyl succinimide, or polyalkenyl succinimide, hydrocarbyl carbonates, such as polybutene alcohol, polybutene chloroformate, polybutene amines formulated in mineral or other carriers, polyisobutylene amine reformulated in polyether carriers, and one-component
15 polyether amines, and the like. Several others have been set forth elsewhere in the specification and are contemplated in gasolines, and other co-fuels.

Applicant's invention contemplates that acceptable deposit control additives will meet industry and regulatory
20 standards, including CARB's 10,000 mile BMW IVD and Chrysler PFI keep clean tests. Thus, contemplated average deposits on all valves cannot exceed 100 milligrams on said BMW test, nor no more than 5% plugging, as measured in flow loss, in any one injector.

25 It is an express embodiment to avoid employing IVD additives or PFI additives, which show any detrimental performance in combustion chamber deposit control or reduction.

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Applicant's invention expressly incorporates a combustion chamber deposit control additive. It is an express object of instant invention to employ deposit additives beyond IVD and PFI additives, namely to employ additives additionally or in lieu of IVD/PFI a combustion control deposit (CCD) additive.

It is an express embodiment to employ additive or other means to reduce and/or control combustion chamber deposition, so as to improve combustion and/or reduce combustion temperature.

Applicant notes that combustion chamber additives are not necessarily novel and have been used to maintain fuel system cleanliness for some time. In the practice of Applicant's invention, especially with higher performing neat ECS fuels, CCD additive is optional.

However, additive and lubricating oil practice, especially in co-fuel practice that reduce or control combustion chamber deposits, are an express embodiment of this invention.

Thus, Applicant's invention expressly contemplates the use of combustion chamber deposition control/deposit modifier additive or additive packages, especially those absent carrier fluid, and which have the effect of reducing octane number increase (ORI) of engines with combustion chamber deposits and/or which reduce and/or are capable of changing the characteristic of combustion chamber deposits.

Applicant's preferred combustion chamber deposit control additives exclude lower molecular weight

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surfactants and high molecular weight polymeric dispersants based upon polybutene. Applicant expressly contemplates employing new classes of additives which control or reduce combustion chamber deposits, and which in the case of gasoline reduce octane requirement increases (ORI), particularly those additives which can reduce existing deposits and/or reduce the ORI below clear base fuel absent said additive, over time.

Non-limiting examples of desireable CCD additives include Shell's VEKTRON ORIC additives (Octane Requirement Increase Control) or ORR additives (Octane Requirement Reduction) and/or similar additive package, or Oronite's CCD (Combustion Chamber Deposit) additive package, Texaco's CleanSystem³ or Ethyl's equivalent HiTec additive package. It is expected other combustion control additives and packages will be developed. Additive concentration levels may range from moderate to very high, depending upon the efficacy of the additive/additive package and co-fuel employed. Other means of controlling combustion chamber deposits include intermittent high concentrations of polyeramines. glycol boarates and ethylene dichloride may be employed.

However, given nature of increased burning velocity and temperature reducing aspects of Applicant's invention, less desireable conventional additives can be employed, absent significantly deleterious adverse combustion chamber deposition.

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Thus, it is preferred that Applicant's combustion chamber deposit control additives, PFI (Port Fuel Injector) and IVD (Intake Valve Deposit) additives, and concentrations thereof, be effective in controlling and preferably reducing existant combustion chamber deposits. It is also preferred that said deposit control additives be in amounts able to enhance the presence of Applicant's ECS compounds and/or metallics, which may be concentrations above or below those recommended.

It is an express embodiment of this invention that a clean combustion additive package be incorporated into any co-fuel and/or ESC fuel composition. It is further contemplated that said combustion additive package incorporate at least one organo manganese compound (preferably MMT) and/or other combustion improving metallic compound (or mixture thereof), and a combustion chamber deposit control/reducing additive (e.g. Shell's VEKTRON ORIC Octane Requirement Increase Control or ORR additive, Oronite's CCD additive package, Texaco's CleanSystem³, or Ethyl's equivalent HiTec additive package).

It is further contemplated this clean combustion additive package may optionally contain one or more injector and/or intake valve deposit additive(s).

Concentrations of each compound or the performance features of individual additives and/or additive package, as an entirety, should meet minimum standards set by industry or requirements established by legal or regulatory standard. It is contemplated that concentrations may

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include those that exceed or be less than those recommended by the additive manufacture.

In the practice of this invention Applicant has found that certain halogen scavengers in combination with certain
5 metallics, notably potassium, may aggravate valve sticking. Thus, it is vital that compatibility of additive and ECS metallic containing fuels be determined prior to use.

Example 185

10 A composition comprised of a minor amount of at least one metallic, including, for example a cyclopentadienyl manganese tricarbonyl compound, and a major amount of a combustion chamber deposit control additive or additiv
package, such as Texeco's CleanSystem³ additive.

15

Example 186

The composition of example 185, wherein the combustion chamber deposit control additive includes, or additionally includes, at least one ECS compound, preferably DMC.

20

Example 187

The composition of examples 185, additionally comprising an injector and/or induction valve deposit control additive; wherein said additives are same or
25 differing additives.

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Example 188

A composition comprising at least one cyclopentadienyl manganese tricarbonyl and/or other combustion improving metallic compound, a combustion chamber deposit reducing additive, and optionally, an injector and/or induction valve deposit control additive; wherein said additives are same or differing additives.

Example 189

A method incorporating the fuel compositions of Examples 185-189, where said additive package is employed deposit reducing quantities in a fuel for combustion in an internal combustion engine; wherein said compression ratio is increased to a compression ratio beyond average conventional compression ratios, or compression ratio's equal to greater than 8.6:1, 8.7:1, 8.8:1, 8.9:1, 9.0:1, 9.1:1, 9.2:1, 9.3:1, 9.4:1, 9.5:1, 9.6:1, 9.7:1, 9.8:1, 9.9:1, 10.0:1, 10.2:1, or greater.

Example 190

A method incorporating the fuel compositions of Examples 185 - 189, where said additive package is employed in deposit reducing quantities in a fuel for combustion in an internal combustion engine; wherein anti-knock sensors do not retard spark advance to avoid knocking, whereby fuel economy and/or power is improved by at least 0.5%, 1.0%, 1.5%, 2.0%, 3.0%, 5.0%, or more, over clear fuel.

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Example 191

The composition of 190, wherein the manganese concentration is equal to an amount such that the treatment level of the additive package equals at least the minimum
5 metallic concentrations for the fuels set forth herein.

Example 192

The composition of 190, wherein deposit control additives are in an amount such that after treatment of a
10 fuel, combustion chamber, injector, and/or intake valve deposits are controlled, modified, or reduced, and/or wherein treated fuel meets regulatory or minimal legal standards.

Thus, Applicant contemplated additive packages will
15 incorporate IVD, PFI and ORI (or CCD) control additives, additive packages and/or mixture thereof.

Example 193

A fuel composition comprising an ECS fuel (comprising
20 an ECS compound, preferably DMC, and at least on combustion improving metallic, preferably MMT); a co-fuel; an injector deposit control additive; an intake valve deposit control additive; and a combustion chamber deposit control additive; wherein said deposit control additive may
25 be same or multiply compound, and/or wherein said compound or compounds change/reduce existing combustion chamber deposits while preferably enhancing combustion efficiency (but not required).

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It is preferred that additives, including deposit control additives, operate to enhance the ECS and metallic combustion chemistry, which represents the predominate thermodynamic and combustion object of Applicant's invention, as opposed to merely enhancing the fuel and combustion characteristics of Applicant's co-fuels.

Thus, given the extremely attractive combustion characteristics of ECS metallic containing fuels, alone, combustion chamber deposits are substantially controlled when employed in combination with a co-fuel, absent need for additional additive.

Greater concentrations of ECS metallic fuels as a percentage of total fuel, when in combination with co-fuels, reduces combustion chamber deposition.

However, as noted it is contemplated that neat ECS fuels contain deposit control additive(s), may include injector, valve intake and/or combustion chamber deposit additive(s). Lubricity, antioxidant, corrosion, and other known additive are contemplated. Non-limiting examples of wax crystal modifiers (wax anti-settling agents) or middle distillate flow improvers include ashless low molecular weight co-polymers and include ethylene vinyl acetate co-polymers. Cold flow improvers are contemplated with diesel fuels, particularly those with reduced sulphur and/or reduced aromatic concentrations, especially as fuel temperatures drop. Betz Process Chemicals markets a superior cold flow improver additive. In the practice of

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this invention cold flow improvers are expressly contemplated.

Non-limiting examples of antifoam agents include polysilicone based compounds. Non-limiting examples of
5 detergents include succinimide, ashless polymeric disperants.

Non-limiting examples of cetane improvers include alkyl nitrates of which 2 ethyl hexyl nitrate is desireable with concentrations of 0.01, 10, 25, 50, 75, 100, 150, 200,
10 250, 500, 750, 800, 900, 1000, 1100, 1200, 1250, 1300, 1400, 1500, 1600, 1750, 1900, 2000 ppm or greater concentrations acceptable. Other concentrations include up to approximately 0.35, 0.40, 0.45, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5 % vol., or
15 more, of the fuel.

Other cetane improvers include Arco's peroxide-based dialkyl peroxide improver, which may be included in the fuel composition up to approximately 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5% vol., or at
20 greater volumes.

Several proprietary ashless long chain polar compounds are currently marketed, which are contemplated in the practice of this invention. Multifunctional additive packages are also contemplated. Such packages may contain
25 detergents, cetane/octane improvers, combustion chamber deposit control additives, fuel stabilizers, flow improvers, anti-foam agents, reodorants, demulifier,

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corrosion inhibitors, lubricity additives, and/or solvents for package stability.

Lubricity additives are particularly contemplated in low/no sulfur diesel/distillate fuels, in order to avoid equipment, elastomer, and other failure.

The operation of lower combustion temperatures in the practice of Applicant's invention unexpectedly serves to reduce the formation of port fuel injector deposits.

10 Example 194

A method of operating an engine at combustion temperatures at least 50°F below same fuel absent ECS compound, metallic, and PFI deposit control additive, wherein said reduced temperature operation after said operation, results in a reduced temperature transfer to fuel remaining in or near the pintle tips of port fuel injector subject to otherwise high soak temperature transfer; wherein the formation of free radicals capable of combination in auto-oxidation, chemical rearrangement and/or degradation of remaining fuel are reduced; and/or wherein sticky deposits and/or degraded fuel acting as deposit precursors are reduced; wherein Port Fuel Injector deposits are controlled and/or flow restriction is less than 10.0%, 9.0%, 8.0%, 7.0%, 6.0%, 5.0%, 4.0%, 3.0%, 2.0%, or less; or alternatively employing a Peugeot XUD-9A/L test for diesel fuel measuring injector coking, shows an air flow rating in excess of 180, 190, 200, 210, 220, 230, 250, 260 ml/minute when needle lift is 0.3 mm.

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Applicant's invention also unexpectedly reduces the increase in NOx emissions and particulates typically occurring from use of such additives in diesel fuel systems.

5 Example 195

 The method of Example 194, wherein the additive optionally contains an intake deposit control additive and/or combustion chamber deposit control additive, wherein said additive or additives are employed in a composition
10 containing a diesel co-fuel, together with balance of combustion and temperature reducing amount of ECS compound(s) and metallic(s), wherein said operation of engine results in reduction of NOx and/or particulate emissions, when compared to said deposit control
15 additive(s) employed in clear diesel co-fuel alone (absent ECS compound and metallic).

 Applicant notes the enhanced combustion burning and temperature reducing properties of instant invention
20 unexpectedly enhance the operating performance features of such PFI, IVD, CCD additive and additive packages.

Example 196

 A method of employing a CCD, IVD or PFI additive in an
25 internal combustion chamber: said method comprising simultaneous injection of an atomized vapor comprising a minor amount of at least one high burning velocity (and/or low combustion temperature causing) ECS compound, at least

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one high energy releasing metallic compound, and a CCD, IVD, or PFI compound, and mixture, and a low sulfur reformulated or conventional co-fuel; combusting said vapor in said combustion chamber, wherein high kinetic energy metallic vapor phase combustion occurs; whereby existing combustion chamber deposits are modified or reduced and/or intake valve deposition is similarly avoided over time, as compared to employing said deposit control additive(s), absent said ECS compound and metallic.

It is further contemplated that the additive packages of instant invention will be formulated to avoid intake valve sticking and crankcase oil contamination.

It is further contemplated that Applicant's IVD, PFI and/or ORI (Combustion Chamber Deposit) control additives meet minimal industry and government tests and/or regulations.

Example 197

A method of avoiding CCD deposits employing an ECS/co-fuel combination; said method comprising: mixing a co-fuel with combustion improving amount of a metallic and a ECS compound (preferably DMC); a combustion chamber deposit (CCD) control additive; and a co-fuel; combusting said fuel in an engine for the equivalent of 5,000, 10,000, 15,000, 20,000, 30,000, 50,000, 75,000, or 100,000 miles, or more; wherein the octane requirement for engine operating on ECS/co-fuel combination does not exceed, or is less, than

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the octane requirement of same engine operating on clear co-fuel alone (but containing same CCD additive).

Example 198

5 The method of Example 197, wherein the octane requirement as measured in (R+M)/2 of said fuel is at least 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or more numbers less than clear co-fuel alone (2 number or greater preferred).

10

Example 199

 The method of Example 198, wherein said engine has operated the equivalent of 15,000, 20,000, 30,000, 50,000, 100,000 miles or more.

15

Example 200

 The method of 199, wherein said engine passes a laboratory test or other test wherein measured combustion chamber deposits or equivalent show less than 300, 250, 200, 180, 160, 140, 120, 100, 80, 60, 40, 20, 10, 5.0, 3.0, 2.5, 2.0, 1.75, 1.5, 1.25, 1.0, 0.75, 0.6, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.125, 0.11, 0.10, 0.09, 0.08, 0.075, 0.06, 0.05, 0.002, 0.001 grams of deposition, or less. Preferred deposition weight is less than less 1.5, 0.9, 0.6, 0.3, 0.15, 0.10 grams, or less, per combustion chamber or equivalent.

25

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Example 201

The method of Example 199-200, wherein intake valve deposit, port fuel injector deposit and gum control additives are employed in sufficient concentrations, wherein intake valve deposits are less than 100, 90, 80, 70, 60, 50, 40 mg under BMW 3181 test (BMW IVD test), and wherein port fuel injector deposits do not exceed a 10%, 9%, 8%, 7%, 6% or 5% or less restriction at 10,000 miles when employing a 2.2 liter Chrysler engine (CRC PFI test), and wherein the maximum gum limits are 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5.0 mg/100 ml or less washed, and/or 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 mg/100 ml or less unwashed.

15 Example 202

The method of Example 201, wherein the engine is a gasoline or internal combustion engine whose compression ratio is 9.6:1, 9.7:1, 9.8:1, 9.9:1, 10.0:1, 10.1:1, 10.2:1, 10.3:1, 10.4:1, 10.5:1, 10.6:1, 10.7:1, 10.8:1, 10.9:1, 11.0:1, 11.1:1, 11.2:1, 11.3:1, 11.4:1, 11.5:1, 11.6:1, 11.7:1, 11.8:1, 11.9:1, 12.0:1, 12.1:1, 12.2:1, 12.3:1, 12.4:1, 12.5:1, 12.6:1, 12.7:1, 12.8:1, 12.9:1, 13.0:1, 13.1:1; 13.2:1, 13.1:1, 13.2:1; 13.5:1, 13.6:1, 14.0:1, 14.1:1, 14.2:1, 14.3:1, 14.4:1, 14.5:1, 14.6:1, 14.7:1, 14.8:1, 14.9:1, 15.0:1, 15.5:1, 16.0:1, 16.5, 17.0:1, 17.5:1, 18.0:1, 18.5:1:1, 19.0:1, 19.5:1, 20.0:1, 20.5:1, 21.0:1, 21.5:1, 22.0:1, 22.5:1, 23.0:1, 23.5:1,

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24.5:1, 25.0:1, 30.0:1, 35.0:1, 40.0:1, 50.0:1, 70.0:1 and compression ratios therein and/or greater.

Example 203

5 The methods and gasoline compositions above, wherein the (R+M)/2 octane of the composition is 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107.

10 Example 204

 The gasoline method, wherein the engine is designed to operate on a gasoline whose octane is equal to or exceeds 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 100, 101, 102, 103, 104, 105, 106, 107, 108 or
15 greater.

Example 205

 The gasoline method, wherein engine operation comprises use of electronic knock sensor to retard spark
20 and wherein spark retardation and hence combustion efficiency is improved over clear fuel by at least 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0. or 4.5 octane numbers or more, after a equivalent of 5,000, 10,000, 15,000, 20,000, 30,000, 50,000 miles or more.

25

Example 206

 The method of Example 205, wherein acceleration of engine employing Applicant's fuel composition with

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combustion chamber deposit control additive is improved 1.0%, 2.0%, 3.0% to 10%, 4.0% to 15.0% or more over the clear fuel, alone.

5 Example 207

 A method of reducing NOx emissions comprising: mixing a combustion improving amount of a metallic with an ECS compounds and optionally with a co-fuel, together with a combustion chamber deposit reducing additive; combusting
10 said fuel, whereby NOx emissions are reduced by at least 5.0%, 7.0%, 10.0%, 15.0%, 20.0%, 25.0% or more, compared to co-fuel absent metallic, ECS compound and combustion chamber deposit control/reducing additive.

 It is additionally contemplated that ECS compounds in
15 their neat form will contain additives, as required. For example, to avoid corrosion and maintain stability, caused by peroxide formation, phenolic-based and amine based stabilizers such as UOP 7 and UOP 5 may be employed in the storage and use of neat ECS compounds or fuels.
20 Concentrations will vary depending upon stability concerns. For example, ETBE and diisopropyl ether have a stronger tendency to form peroxides than does MTBE and hence require greater concentrations.

 In the case of carbonates, especially DMC, when
25 exposed to water for extended periods, due to hydrolysis, decomposition into methanol may occur, hence leading to corrosion concerns. Thus, water reducing agents, salts, co-solvents, demulsifiers, anti-oxidants, stabilizers,

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corrosion inhibitors, and the like are expressly contemplated.

Mitigation Practice

5 It is contemplated that Applicant's neat ECS fuels, neat co-fuels (absent ECS and/or metallics), and/or ECS and/or metallic co-fuel combinations, will employ certain mitigation practices, as required. Mitigation practices include vapor pressure reduction (VPR), flash point
10 temperature increase (FPI), hydroscopic/phase separation control, and the like. Co-solvent usage is also contemplated to reduce evaporative emissions.

 Lower molecular weight ECS alcohol compounds are hydroscopic and tend to phase separate in fuel systems
15 exposed to or containing water. Thus, co-solvents that control phase separation are desirable.

 Certain carbonates, namely di-methyl and di-ethyl carbonates are prone, in certain circumstances, to hydrolyze when exposed to similar environments. Low
20 molecular weight ECS alcohols, ethers, carbonates, ketones, and the like, can adversely increase vapor pressure or reduce flash point temperature. Their useage can also reduce T-50 temperatures causing driveability problems or technical enleanment. Correction of T-50 and end boiling
25 point adjustment employing azeotroping co-solvents is known in the art, see my EPO Patent 8690642.6.

 In the practice of this invention a different and unique class of co-solvents and means are contemplated to

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mitigate vapor pressure and flash point problems, particularly in fuels heavier than gasoline, e.g. jet turbine, gas oil turbine, diesel fuels, and the like.

5 It is generally preferred that co-solvents be ECS compounds or have ECS combustion/temperature enhancing attributes. Thus, It is preferred that Applicant's co-solvents (independent of ECS and/or metallic effect) generally increase the resultant fuel's LHV and/or burning velocity, especially in co-fuel applications.

10 It is contemplated that Applicant's co-solvents include inorganic and/or organic compounds. In FPI or VPR applications, especially when an ECS compound is present (or alternatively in fuels absent ECS or metallic), it is preferred that the co-solvent(s) have a vapor pressure of
15 1 mm, or less, at temperatures of -20, -10, 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140°C, or greater.

It is also desireable that Applicant's co-solvent(s), especially when employed for FPI, have flash point
20 temperature of at least 60, 80, 100, 110, 120, 130, 140, 160, 180, 200, 210, 230, 240, 260, 280, 300, 320, 330, 350, or 360°F.

It is desireable that Applicant's co-solvents be flammable. It is preferred that they be preheated before
25 ignition, or moderately heated and exposed to high ambient temperature, or easily ignited under almost all ambient temperature conditions. Complete or substantially complete decomposition at combustion and pre-combustion temperature

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is preferred. It is desirable the co-solvent have as many of the combustion burning velocity and temperature reducing features of ECS compounds as possible.

5 In certain applications, the co-solvent should not be water soluble. However, when hydrolysis and/or phase separation occur due to presence of water or acidity, a water soluble co-solvent can be advantageous.

10 It is desirable that a synergistic relationship exist between the ECS compound(s) when employed, and the co-solvent(s). It is expressly contemplated that multiple co-solvent mixtures be employed.

In other words, differing requirements can be satisfied with differing co-solvents, and mixtures thereof.

15 In other words, one or more co-solvent may be employed for phase separation control, and one or more for FPI or VPR, one or more for reducing freezing temperatures. While there is no limitation on the number or ranges of co-solvents in a mixture, Applicant recognizes that differing fuels requirements will elicit differing co-solvent mixtures. When practical single component co-solvent mixtures are preferred.

25 Co-solvent practice may also be supplemented or substituted by use of heavy napha's, including aromatic napha's. Thus, it is an embodiment to employ heavy or moderately heavy hydrocarbons, including naphas, in lieu of or in addition to co-solvent(s), as means for FPI and VPR.

It is an express embodiment of this invention that use of Applicant's co-solvents in fuel combinations will

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provide increases in flash point or reductions in vapor pressure that are arithmetic and those greater than the arithmetic effect of their combination. Co-solvent cost, ease of use, considerations of toxicity, availability, ECS properties, and the like, must be weighted in such considerations.

Therefore, while not required, it is an embodiment that vapor pressure reductions and/or increases in flash point temperature, and/or reductions in average fuel melting temperatures exceed the sum of the individual co-solvent, ECS compound (if employed), and/or co-fuel components.

It is an express embodiment to employ Applicant's co-solvents in neat ECS and/or metallic fuels, alone. It is also an embodiment to employ such co-solvents in clear fuels (co-fuels), which are absent ECS compound or metallic; or employ such co-solvents in co-fuels, which may contain ECS compound and/or metallic.

It is also preferred that co-solvent usage not increase melting/freezing point temperatures, or diminish or aggravate fuel stability, corrosion, elastomer deterioration, evaporative emissions, toxic emissions, hazardous combustion emissions, or combustion burning velocities and combustion temperatures. It is also preferred the co-solvent usage not contribute to gumming or oxidation.

However, in such circumstances, (e.g. for example, where freezing points are not sufficiently low), it is

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contemplated an additional co-solvent, substitute co-solvent, additional additive, or other means may be employed.

Co-solvents that cause elastomer swelling or deterioration, corrosion or fuel degradaton may be corrected by employing additional agents, e.g. corrosion inhibitors, anti-oxidants, etc. However, Applicant's preferred co-solvents do not cause such problems.

Applicant's desired co-solvents will have melting points less than 20, 10, 0, -5, -10, -15, -20, -25, -30, -40, -50, -60, -70, -80, -90, -100, -130, -140°C, or below. Preferred will be those with melting points less than -5°C, more preferably less than -40, -50, -60, -70, -80, -90°C, or below.

Applicant's co-solvents will have boiling points above 70, 80, 90, 100, 110, 120, 300°C, and greater. Boiling points above 130, 160, 190, 200, 220, 240, 260, 270°C, or greater, are preferred.

Desired flash point temperatures of co-solvents are greater than --0, -31, -20, -15, -10, -5, 0, 5, 10, 15, 20, 25, 30, 35, 38, 40, 50, 58, 60, 65, 70, 75, 80, 85, 90, 95, 100, 120, 130, 140, 150, 160, 170, 180°C, or greater. Preferred flash point temperatures are those in excess of 40, 60, 80, 100, 120, 130, 140, 150°C, or more. More preferred are those above 80, 100, 120, 150, 170°C.

Applicant's desirable cosolvents have a latent heat of vaporization in excess of 18, 20, 21, 23, 24, 25, 27, 29, 30, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57,

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59, 62, 65 $\Delta_{\text{vap}}H(T_b)/\text{kJ mol}^{-1}$ (or equivalent). It is preferred that co-solvent LHV's be greater than any co-fuel to which they might be added. However, LHV must be balanced by the other aspects of usage, e.g. LHV of resultant fuel, LHV effect of ECS compound (if any), flash point and/or vapor pressure priority, etc. Applicant's preferred LHV's are equal or above 28, 30, 32, 34, 38, 40, 45, 50, 55, 60 $\Delta_{\text{vap}}H(T_b)/\text{kJ mol}^{-1}$ (or equivalent).

Applicant's desired co-solvents, especially for vapor pressure reduction and/or flash point improvement, will have moderate, to very low, to exceptionally low vapor pressures. Albeit moderate vapor pressure may be acceptable in certain circumstances.

It is desirable that Applicant's co-solvent have a vapor pressure of 1 mm at temperature greater than -20, -10, 0, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 160, 180°C, or greater. Preferred co-solvent temperatures at vapor pressures of 1 mm should exceed 20, 40, 60°C. More preferred temperatures are those that exceed 80, 100°C, or more.

Azeotrophening co-solvent(s) may be employed, however in cases where flash point improvement is sought, azeotrophening is less preferred. Thus, the co-solvent lower molecular weight alkyl alcohols, are generally less preferred.

Applicant has found hydrocarbon soluble, flammable glycols, ketones, and their acetates, and esters to be desirable. Ethanoic, propanoic, butanoic, pentanoic, and hexanoic acids, including their acetates, esters and ethers

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are also desireable. Ethenes, butenes, propenes, hexenes, pentenes are acceptable.

The specie or compound classifications found herein are not intended to be limiting. Applicant contemplates co-solvents, which may be outside any disclosed herein, and further comtemplates his preferred co-solvents may include any species, subspecies or homologue or analogue of any disclosed species, compound, or group herein, under the proviso said co-solvent(s) meet the functional requirements set forth herein.

It is desireable that the co-solvent be soluble with the targeted ECS compound, if employed, and optionally with water.

Applicant's co-solvents may be selected from a very broad class of flammable chemistry. Applicant's desired co-solvents are those having less than 22, 20, 18, 16, 14, 13, 12, 11, 10 or 9 carbon atoms, with those having less than 8, 7, 6, 5, 4, 3, 2 or single carbon atoms being preferred. While those above these ranges are contemplated and acceptable, those having 7, 6, 5, 4, or fewer carbons in a chain are also preferred. Co-solvents containing oxygen are desireable. Co-solvents containing OH radicals are also desireable. Applicant has found that co-solvents having molecular structure in part comprising CH₃CO₂, and/or OH to be desireable. Applicant has also found that nonvolitile, nonion producing co-solvents to be desireable for purposes of reducing vapor pressure and/or raising flash points.

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Non-limiting examples of Applicant's co-solvents include: alcohols, glycols, ketones, esters, phenols, acetals, acid azides, acid halides, acids and acid derivatives (aldehydic, aliphatic dicarboxylic, aliphatic monocarboxylic, aliphatic polycarboxylic, amino acids, hydroamic, hydroxyacids, imidic, ketonic, nitrolic, orthoacids, peracid, etc.), acetic acids, acetic anhydrides, acetic acid esters, aldehydes, aliphatic hydrocarbons (including high boiling point naphthas), amides, amidines, amidoximes, anhydrides, aromatic hydrocarbons, azides, azines, azelates, azo compounds, betaines, bromoacetaldehydes, bromoethanes, bromoethylenes, bromoacetic acids, bromobutanes, bromobutenes, bromobutylenes, bromo ethers, di bromo compounds, butyric acids, butanoic acids, butanoic esters, esters, orthoesters, ethers, glycols, ethylene glycols, di-ethylene glycols, diethylene glycol ethers, diethylene glycol acetates, propylene glycols, propylene glycol esters/ethers, di-propylene glycols, glycol ethers, triethylene glycols (including acetates, diacetates, esters, ethers, and amines thereof), tetraethylene glycols (including acetates, diacetates, esters, ethers, and amines thereof), tripropylene glycols, tetrapropylene glycols, di-butylene glycols, tributylene glycols, tetrabutylene glycols, pentaethylene glycols (including acetates, diacetates, esters, ethers, and amines thereof), glyceric acids, glycerols, formates, carbinols, carbitols, nitriles, acetates, ethylene acetates, esters, hydrates, hydrides,

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ether tetraethylene glycol, tetraethylenepentamine, tripropylene glycol, tetrapropylene glycol, dipropylene glycol, propylene glycol monomethyl ether, ethylene glycol monomethyl ether, ethylene glycol monopropyl ether, propylene glycol monopropyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, propylene glycol, ethylene glycol, hexylene glycol, dipropylene glycol, diethylene glycol, tripropylene glycol, tetraethylene glycol, tetramethylene glycol, tetrapropylene glycol, polyethylene glycol (200, 300, 400, 600, 1000, 1500, 1540, 4000, 6000 Ashland Chemical), polyethylene glycol 3350 (Spectrum), polypropylene glycol (P400, P1200, P2000, P4000 Ashland Chemical), cyclohexylamine, dibutylamine, diethylamine, diethylenetriamine, diethylethanolamine, diisopropanolamine, morpholine, triethylamine, triethylenetetramine, triisopropanolamine, toluene, amino methyl propanol, propylene oxide, propylene glycol, 1,2 propanediol carbonate, salicylic acid, succinic acid, tartaric acid, tannic acid, 2,2,4-trimethylpentane, dimethylbenzenes, dimethyl formamide, n-methyl-2 pyrrolidone, amyl alcohol (primary), cyclohexanol, 2-ethylhexanol, methyl amyl alcohol, tetrahydrofurfuryl alcohol, TEXANOL ester alcohol (Eastman Chemical), UCAR Filmer IBT (Union Carbide Corp.), amyl acetate, dibase ester, ester solvent EEP (Ashland Chemical), 2-ethylexyl

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acetate, glycol ether acetates (DB, DE, DPM, EB, EE, PM, Ashland Chemical), isobutyl acetate, isobutyl isobutyrate, n-pentyl propionate, cyclohexanone, 2-hexanone, 3-hexanone, 2-methyl-3-pentanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, 3,3-dimethyl-2-butanone, diactone alcohol, diisobutyl ketone, ethyl methyl ketone, pinacolone, methone, 3,3-diphenyl 2-butanone, 1-hydroxy 2-butanone, 3-hydroxy-(dl) 2-butanone, 3-methyl 2-butanone, oxime 2-butanone, 2-butanone, 2-methyl propanoic acid, cyclopentanone, cyclopropyl methyl ketone, 2-tetrahydrofurylmethanol, cyclohexanone, isophorone, methyl amyl ketone, methyl isoamyl ketone, acetonylacetone, acetic anhydride, benzyl alcohol (a-hydroxytoluene) and variations, triisobutylene, tetraisobutylene, allylidene diacetate, acetol, 1 (4-methoxyphenyl)-2-propanone, isobutyrophenone, acetonylbenzene, butyl acetate, C-4, C-4+ aliphatic alcohols, n-butylbutyrate, cetyl alcohol, cyclohexane, cyclohexanol, cyclohexanone, diethylphthalate, 2,5 dimethoxytetrahydrofuran, p-dioxane, 1,3-dioxane, 1,4-dioxane, 5-hydroxy-2-methyl-1,3-dioxane, glycol methylene ether, propylene carbonate, isopropylene carbonate, glycerin, 1,2,3-propanetriol, heptane, n-hexane, 2-methylpentane, 3-methylpentane, methycyclopentane, 1,4-benzenediol, isopentyl alcohol, methyl ethyl ketone, 4-methyl-2-pentanone, methyl propyl ketone, diisopropyl ketone, 1- or 3- or 4- or 5 hydroxy 2-pentanone, diisopropyl ketone, methyl propyl ketone, diacetone

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hydroperoxides, hydroxamic acids, hydroxyacids, imides, imidic acids, imines, ketenes, lactams, lactones, glycolic acids, butyric acids, heptic acids, valeric acids, isocaproic acids, nitrolic acids, nitrosolic acids, octanoic acids, esters of octanoic acids, onium compounds, orthoacids, ortho borates, octynes, octenes, octanones, oximes, esters of oxalic acid, oxalic acids, ethanoic acids, esters of ethanoic acids, esters of nonanoic acids, propanoic acids, esters of propanoic acid, pentanoic acids, propanediones, propanones, ethenes, propenes, butenes, pentanes, petenes, hexenes, esters of pentanoic acids, butanoic acids, oxalic esters, esters of butanoic acids, pentaneic acids, esters of pentaneic acids, pentanedioic acids, esters of pentanedioic acids, 2- or 3-pentanones, hexanoic acids, esters of hexanoic acids, heptanoic acids, esters of heptanoic acids, esters of formic acid, glycol esters, octenes, octanone(s), oxalic acids, esters of oxalic acids, esters of hexanoic acid, hexanones, toluene bromides, toluene cresols, toluene dimethyl amino compounds, toluene ethers, toluene oxyls, pentanediols, peroxides, furans, esters of 2-furancarboxylic acids, furfurals, propenes, propenoic acids, esters of propenoic acids, ethers, butenedioic acids, bromo-alcohols, ethanetriols, propanetriols, butanetriols, pentanetriols, naphthalenes, hexanetriols, septanetriols, octanetriols, nitrobenzene, iodobenzene, 2-nitrophenol, and the like.

Nitrogen based compounds are also acceptable, depending upon the application. However, Fluorine,

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chlorine, sulphur, phosphorous based, and other toxic compounds, now known or later determined, should be avoided. Non-carbon based co-solvents are also expressly contemplated. Solid co-solvents, which may be dissolved by mutual solvent, are contemplated. Co-solvent chemical structure is not limited, and may be cyclic, bi-cyclic, aromatic, non-aromatic, branched or straight chain, or combination thereof.

It is preferred that the co-solvent be thermally stable, not decompose under normal handling and operating temperatures, and not cause co-fuel deterioration, e.g. gumming, corrosion, etc. It is additionally desirable that the half life of its evaporative or combustion product be very short, preferably less than days (e.g. 8, 5, 4 or less), more preferably less than hours (e.g. 24, 18, 12, 8, 4, 3, 2, 1 or less), most preferably less than minutes (e.g. 60, 45, 30, 15, or less).

Non-limiting examples (to also include homologues and analogues thereof) are: triethylene glycol, 3-aminopropyl ether triethylene glycol, diacetate triethylene glycol, monobutyl ether triethylene glycol, monomethyl ether triethylene glycol, monopropyl ether triethylene glycol, tetraethylene glycol, dibutoxytetraethylene glycol, diacetate tetraethylene glycol, aminopropyl ether tetraethylene glycols, monobutyl ether tetraethylene glycol, monomethyl ether tetraethylene glycol, dimethyl ether tetraethylene glycol, diethyl ether tetraethylene glycol, monoethyl ether tetraethylene glycol, monopropyl

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alcohol, isopentyl phenyl ketone, 2-pentanone, diacetone
alcohol, isopentyl phenol ketone, n-butyl phenol ketone, i-
butyl phenol ketone, 2-butyl phenol ketone, isopropyl
acetone, 2- or 3- or 4-methoxy phenol, dihydrate oxalic
5 acid, pentane, phenol, 3-methoxy phenol, 1,2 or 1,3 or 1,4
or 2,4 or 2,5 or 2,6 or 3,4 or 3,5 dimethyphenol, 1-octene,
isobutyl 2-methylpropanate, 2-phenoxyethanol, diethyl
carbitol, methyl carbitol, butyl carbitol, methyl ethyl
carbinol, ethylene glycol, ethylene acetate, ethyl acetate,
10 acetophenone, benzyl acetate, 1,3 or 1,4 or 2,3
butanediol, ethylene glycol, formaldehyde, formamide,
triethyl ester orthoacetic acid, trimethyl ester
orthoacetic acid, oxalic ester (diethyl ester oxalic acid),
methyl hydroperoxide, ethyl hydroperoxide, acetyl peroxide,
15 ethyl peroxide, di(tert-butyl) peroxide, acetic anhydride,
2-ethyl butyl ester acetic acid, cresyl acetates,
methylglycolate, methylester phenoxy acetic acid, nitril
acid, butyric acid, butanoic acid, 2-butyl butanoic acid,
2-ethyl butanoic acid, tert-butyl butanoic acid, butyl
20 nitril, propyl ester butanic acid, diethyl acetic acid,
acetoneacetic acid, allyl acetoneacetate, diacetylacetone,
acetylacetone, ethyl ester benzoic acid, butanic methyl
ester, butanic ethyl ester, butanic propyl ester, isoamyl
butyrate, propyl ester butanoic acid, hexyl ester butanoic
25 acid, 2-methyl-(d) butanoic acid, 2-methyl-(dl) butanoic
acid, ethyl ester 3-methyl butanoic acid, methyl ester 3-
methyl butanoic acid, isopropyl ester 3-methyl butanoic
acid, 2, 2-dimethyl butanoic acid, allyl ester butanoic

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acid, amide butanoic acid, N,N-dimethyl butanoic acid,
anhydride butanoic acid, butyl ester butanoic acid, pentyl
ester butanoic ester, propyl ester butanoic acid,
diethylacetic acid, 2-methyl-(d) butanic acid, methyl
5 acetoacetate, ethyl acetoacetate, diethyl acetal, acetate,
acetyl acetone, 2,2-dimethyl ether ester propanoic acid, 2-
oxo ethyl ester propanoic acid, 2-oxo methyl ester
propanoic acid, 2-oxo isobutyl propanoic acid, 2-oxo-
isopropyl propanoic acid, methyl ester propanoic acid,
10 ethyl ester propanoic acid, propyl ester propanoic acid,
propanoic acid, glyceric acid, 1, 2 dimethoxethane, 1,2
ethanediol, 1,3 butanediol, 2,3 butanedione, 1,2,3
butanetriol, 1,2,4 butanetriol, glutaric acid, glutaric
anhydride, glutaronitrile, 1,5 pentanedial, glutaraldehyde,
15 2,4 pentadione ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), pentanic acid, levulinic
acid, ($\text{CH}_3\text{COCH}_3\text{COCO}_2\text{H}$), dimethyl suberate, octanedioic acid,
1,2,3 pentanetriol, 2,3,4 pentanetriol, formamide,
bromoacetic acid, acetamide, pyruvic acid, methyloxyacetic
acid, propionamide, allyl bromide, diethyl acetal propenal,
20 diacetate propenal, propenal, 1,2 propanediol, 1,3
propanediol, glycerol, trimethyl ether glycol,
acetylpropionyl, acetylacetone, propionic acid,
methyloxyacetic acid, propionamide, maleic anhydride, eis-
crotonic acid, dimethyl oxalate, isobutyric acid,
25 hydroxyisobutyric acid, ethylene glycol, diethylene glycol,
diacetate diethylene glycol, diethyl ether diethylene
glycol, dioleate diethylene glycol, monobutyl ether
diethylene glycol, mono (2 hydroxylpropyl) ether diethylene

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glycol, monobutyl ether diethylene glycol, monopropyl ether diethylene glycol, monomethyl ether diethylene glycol, monomethyl ether acetate diethylene glycol, monoethyl ether diethylene glycol, ethanetriols, propanetriols, butanetriols, pentanetriols, hexanetriols, septanetriols, 1,2,3 butanetriol, 2,3,4 pentanetriol, 1,2,3 pentanetriol, 1,2,3 propanetriol, dioxypentane, 2,4-dioxypentane, hexanetriols, monobutyl ether triethylene glycol, propanoic acid, anhydride propanoic acid, butyl ester propanoic acid, ethyl ester propanoic acid, pentyl ester propanoic acid, octyl ester propanoic ester, pimelic acid, suberic acid, azelaic acid, methacrylic acid, dibromobutanes (e.g. 1,2; dl-2,3; 1,4; meso-2,3; etc), tribromobutanes (e.g. 1,1,2; 1,2,2; 2,2,3; etc.), diacetamide, di(2-bromoethyl) ether, 2-ethylhexanol, furfuryl alcohol, 2-propanone, 2-propen-1-ol, ethyl methanate, methyl ethanate, pentadioic acid, pentadioic acid diethyl ester, pentadioic acid dimethyl ester, pentadioic acid dinitril, 2,3-pentadione, 2,4-pentadione, 1,2,3-pentanetriol, pentanoic acid, pentanoic acid methyl ester, pentanoic acid butyl ester, pentanoic acid ethyl ester, pentanoic acid furfuryl ester, pentanoic acid hexyl ester, pentanoic acid nitrile, pentanoic acid octyl ester, pentanoic acid pentyl ester, carbinol, butyl carbinol, diethyl carbinol, methyl n-propyl carbinol, dimethyl isobutyl carbinol, ethyl isopropyl carbinol, ethyl isopropyl methyl carbinol, diisopropyl carbinol, triethyl carbinol, isoamyl carbinol, dimethyl n-propyl carbinol, 2-butyl methyl carbinol, methyl isobutyl

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carbinol, diethyl methyl carbinol, methyl propyl ketone, methyoxacetic acid, acetoacetic acid, methyl acetate, tert-amyl acetate, ethyl acetate, glycol diacetate, 1,2-propendiol carbonate, 1,2-propanediol, 1,3-propanediol, adiponitrile, 2-amino-2-methyl-1-propanol, triethylenetetramine, benzaldehyde, benzin, benzene, toluene, benzl alcohol, butyl acetate, dimethylaniline, di-n-propylaniline, methyl isobutyl ketone, n-amyl cyanide, di-n-butyl carbonate, diethylacetic acid, diethyl formamide, diisobutyl ketone, ethyl benzoate, ethyl phenylacetate, heptadecanol, 3-heptanol, n-heptyl acetate, n-hexyl ether, methyl isopropyl ketone, 4-methyl-n-valeric acid, o-phenetidine, tetradecanol, triethylenetetramine, 2,6,8-trimethyl 4-nonanone, ethanedial, carbonate 1,2-ethanediol, diacetate 1,2-ethanediol, dimethyl ether 1,2-ethanediol, dinitrate 1,2-ethanediol, n,n-di-methyl formic acid, n,n-di-ethyl formic acid, butyl ester formic acid, isoamyl formate, octyl ester formic acid, pentyl ester formic acid, propyl ester formic acid, isobutyl ester formic acid, propargyl acetate, 2-methoxyethanol, cyclopentanone, cyclopropyl methyl ketone, ethyl propenoate, 3-methyl-2-butanone, phenol, 2-or 3-or 4-methoxyphenol, propanoic anhydride, cyclohexanone, 4-methyl-3-penten-2-one, 2- or 3- Hexanone, [2, 3 or 4]-methyl-[2 or 3]-pentanone, 2-heptanone, methyl phenyl ketone, diethyl benzene, and azulene.

Wide ranges of co-solvent mixtures, including mixing two or more, are expressly contemplated. Thus, any two or

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more co-solvents may be employed jointly, in same or differing proportions.

Varying proportions of different co-solvents will often elicit differing response. For example, it is an embodiment of this invention to employ the same or varying proportions for individual co-solvents of the same general class, or for different classes.

It is an embodiment to employ multiple co-solvents, in same or differing proportions, having different freezing points, flash points and/or vapor pressures, LHV, and burning velocities. One such combination would embody combining one or more moderate to high freezing temperature co-solvent(s) having moderate to high flash point temperatures and a low to very low freezing point co-solvent(s), whereby resultant mixture would have combination of moderately high to high flash point and low freezing point.

It is an embodiment to combine high flash point co-solvent(s) with alcohol and/or other co-solvent to control hydrolysis and/or hydroscopic phase separation. It is also an embodiment that a co-solvent or mixture of co-solvents, which for example act to reduce vapor pressure or elevate flash point, etc., may also act as a mutual solvents to dissolve non-soluble or moderately miscible co-solvent and/or ECS compound(s), if employed.

Applicant recognizes that a wide variety of combinations and mixtures and proportions exist, which acheive the multiple objects of Applicant invention. Thus,

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it is an express embodiment of this invention that co-solvent combinations and mixture exist between individual co-solvents of any one class; between classes of co-solvents; between classes of co-solvent(s) and classes of
5 ECS compounds; between co-solvent(s) and co-fuels; between co-solvent(s), ECS compounds, and co-fuel(s), and/or the like.

Example 208

10 A moderate to high flash point fuel: comprising an ECS compound (preferably DMC), optionally a metallic, and at least one flash point increasing flammable co-solvent selected from fuel soluble polymethylene glycols, polyethylene glycols (including tetraethylene glycols,
15 triethylene glycols, propylene glycols, diethylene glycols), acetates, glycol acetates, ketone acetates, ethylene acetates, ethylene diacetates, di-ethylene acetates, benzyl alcohols, acetic anhydrides, phenol, and/or other nonvolatile, nonion producing co-solvent,
20 homologues, analogues, or mixture thereof; and optionally a co-fuel; under the proviso that if co-fuel is employed the resultant fuel meets co-fuels ASTM or government specifications, including minimum flash point temperature.

25 Example 209

A co-solvent composition, or ECS/co-solvent composition, characterized as being soluble in liquid hydrocarbon fuels, flammable and having a melting point

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less than 20, 10, 5, 0, -5, -10, -20, -30, -40, -50, -60, -70, -80, or -90°C; a boiling temperature equal to or greater than 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 270, 280, 300°C; optionally soluble
5 in water; having a laminar burning velocity in excess of 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, 60 cm/sec; a latent heat of vaporization in excess of 23, 25, 27, 29, 31, 33, 35, 37, 39, 41, 43, 45, 47, 49, 51, 53, 55, 57, 59, 62, 65 $\Delta_{\text{vap}}H(T_b)/\text{kJ mol}^{-1}$ (or equivalent); a vapor
10 pressure of 1 mm at a temperature greater than -30, -25, -20, -15, -10, 0, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, or 140°C; and optionally a flash point temperature of at least 40, 60, 80, 100, 120, 130, 150, 170, 180, 200, 220, 250°F, or greater; and optionally a freeze point equal
15 to or less than 30, 20, 10, 0, -10, -20, -30, -40 (-40°C), -50, -60, -80, -90°F, or less.

Example 210

A high flash point, low freezing temperature co-
20 solvent composition comprising one or more fuel soluble and flammable triethylene glycol compounds, tetraethylene glycol compounds, or other high flash point co-solvent(s), or mixture thereof; and a fuel soluble, flammable, freezing
point reducing agent or co-solvent selected from butyl
25 carbitol, carbinols (including diisopropyl, dimethylene n-propyl, isoamyl, etc.) 1-octene, 4-octene, 1-octyne, 4-octyne, glycol ethers, ethylene glycols, diethylene glycols, diisopropyl ketone, methyl propyl, diacetone

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alcohol, isopropyl acetone, diisobutyl ketone, cyclohexanone, isophorone, or other co-solvent having moderate to moderately high flash point and low to extremely low freezing point, or mixture thereof; whereby
5 the composition's flash point exceeds 60, 80, 100 (38°C), 120, 140, 160, 180, 200, 220, 240, 260°F, and whereby freezing temperature is equal to or less than -10, -20, -30, -40 (-40°C), -50, -60, -80, -90°F, or less.

10 Example 211

The example 210, wherein at least one co-solvent compound is a tetraethylene glycol, triethylene glycol, 1-octene, high flash point ketone, isopropyl acetone, diisopropyl acetone, diisopropyl diacetone, diethylene
15 acetate, diethylene diacetate, or ethylene acetate compound, phenol, (including derivatives thereof) or mixture; and whereby the resultant fuel has an average LHV of at least 28, 30, 32, 34, 35, 38, 40, 42 $\Delta_{\text{vap}}H(T_b)/\text{kJ mol}^{-1}$.

20 Example 212

The composition of Example 210, additionally containing an ECS compound (preferably DMC), and optionally a metallic; whereby the composition's flash point equals or exceeds 100, 130, 150°F, or more, and the freeze point is
25 less than -40°F (-40°C), -47°F (-44°C), -50°F (-46°C), or less; and optionally a latent heat of vaporization equal to or exceeding 28, 30, 32, 34, 38, 40, 45 $\Delta_{\text{vap}}H(T_b)/\text{kJ mol}^{-1}$ (or equivalent).

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Example 213

The example 211, wherein the volume ratio of ECS compound to co-solvent(s) ranges from 20:1, 15:1, 10:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:8, 1:10 with ratio's greater than 1:1 desirable (ratio's of 2:1, 3:1 being desirable and those greater than 10:1, 8:1, 6:1, 5:1, 4:1 preferred).

Example 214

The example 213, wherein the above example fuels additionally comprise a co-fuel; whereby resultant fuel meets all ASTM and/or government specifications, including fuel volatility, e.g. RVP and flash point.

Example 215

The example of 214, wherein the co-fuel is a conventional or reformulated gasoline, whose vapor pressure RVP exceeds 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0 psi, or more, and whereafter combination with co-solvent or mixture of co-solvent (as set forth above), resultant fuel's RVP is equal to or less than 8.0, 7.5, 7.0, 6.5 psi, or less.

Example 216

An aviation jet turbine co-fuel, including Jet A, A-1 or B; or a #1-D diesel, low sulfur or normal grade; or a gas turbine fuel oil # 1-GT, @ 2-GT; said co-fuel

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5 additionally comprising a combustion improving amount of an ECS compound (preferably DMC) having a flash point of less than 38°C, and optionally at least one metallic (preferably MMT), and a flash temperature increasing amount of a co-solvent (preferably a fuel soluble flammable polyene glycol, ketone, acetate, phenol, and/or ester having flash point in excess of 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300°F), wherein resultant fuel is characterized as having a flash point temperature of at least 100°F (38°C).

10

Example 217

15 An #2-D diesel fuel oil co-fuel, normal grade or low sulfur; said fuel additionally comprising a combustion improving amount of an ECS compound (preferably DMC) having a flash point of less than 52°C, an optionally a metallic, and a flash temperature increasing amount of a co-solvent, wherein resultant fuel is characterized as having a flash point temperature of at least 52°C; optionally a reduced cloud or freeze point; and optionally improved viscosity.

20

Example 218

25 An #4-D diesel fuel oil co-fuel, normal grade or low sulfur; or #4, #5 light or #5 heavy fuel oil; or #3 GT gas turbine fuel oil; said fuel additionally comprising a combustion improving amount of an ECS compound (preferably DMC) having a flash point of less than 55°C, a metallic, and optionally a metallic, and a flash temperature increasing amount of a co-solvent, wherein resultant fuel is

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characterized as having a flash point temperature of at least 55°C.

Example 219

5 A #4-GT gas turbine fuel oil co-fuel; said fuel additionally comprising a combustion improving amount of an ECS compound (preferably DMC) having a flash point of less than 66°C, and optionally a metallic, and a flash temperature increasing amount of a co-solvent, wherein
10 resultant fuel is characterized as having a flash point temperature of at least 66°C.

Example 220

 An aviation gasoline co-fuel; said fuel additionally
15 containing a combustion improving amount of DMC or other ECS compound(s) including those having blending vapor pressure greater than 7.0 psi (49 kPa), and wherein said ECS optionally has laminar flame velocity exceeding aviation gasoline (reported at 44.8 cm/sec) or 45, 46, 47,
20 48, 49, 50 cm/sec, or greater; optionally a metallic; a vapor pressure reducing amount of a co-solvent, wherein said resultant aviation gasoline fuel is characterized as having a vapor pressure of at least 5.5 psi (38 kPa) at but not greater than 7.0 psi (49 kPa), and wherein
25 resultant fuel meets all ASTM D 910 specifications.

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Example 221

A marine gas turbine co-fuel; said fuel additionally comprising a combustion improving amount of an ECS compound, preferably DMC, and optionally a metallic, and a
5 flash temperature increasing amount of a co-solvent or mixture of co-solvents, said resultant fuel is characterized as having a flash point temperature of at least 60°C.

10 Example 222

The above examples wherein the co-solvent is comprised of at least one fuel soluble, flammable triethylene glycol, tetraethylene glycol, including mixtures.

15 Example 223

The above examples, wherein the resultant fuels are additionally characterized as meeting ASTM, industry or government standards present and future.

It is also an embodiment of Applicant's invention to
20 employ salts for purposes of mitigating vapor pressure and/or to increase flash point temperatures. It is contemplated that salts may be employed where they are soluble directly into the fuel or indirectly soluble via mutual solvent (e.g. a co-solvent). Most salts are
25 soluble in aqueous solutions and Applicant's invention includes method of employing such solutions directly into fuel, either by separate injection, emulsions, or co-solvent.

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However, mutual solvents are the more preferred practice. For example, many vapor pressure reducing salts are soluble in ketones, including acetone, glycols, ethers, alcohols, and the like.

5 Desired salts are those that do not adversely effect combustion or the emissions of a given fuel and, which in combination with Applicant's ECS fuel and optional metallic, operate to reduce vapor pressure and/or enhance combustion.

10 Acceptable salts are wide ranging. Non-limiting examples include calcium salts (e.g. $\text{Ca}(\text{NO}_3)_2$, CaBr_2), barium, boron salts (e.g. H_3BO_3), potassium salts (e.g. KNO_3 , KBrO_3 , KNO_2 , KHCO_3 , $\text{K}_2\text{C}_2\text{O}_4$, KI , KH , K_2WO_4 , K_2CO_3 , KOH), lithium salts (e.g. LiNO_3 , LiBr , LiI , LiOH), iron
15 salts, aluminum salts, cobalt, magnesium salts (e.g. MgNO_3 , MgBr_2), sodium (e.g. NaNO_3 , NaOH , NaNO_2 , NaHCO_3 , NaBrO_3 , NaBr , NaI , Na_2CO_3 , Na_2WO_4), nitrogen salts (e.g. NH_4NO_3 , NH_4Br , NH_4I), nickel salts (e.g. $\text{Ni}(\text{NO}_3)_2$) and zinc salts (e.g. $\text{Zn}(\text{NO}_3)_2$).

20 Applicant has found that calcium, barium, boron, potassium, magnesium, nickel, and lithium salts to be desireable, especially those soluble directly into hydrocarbons fuels, indirectly via a mutual solvent (co-solvent, e.g ketones), and which can be added to the
25 composition in sufficient quantities to reduce vapor pressure.

Applicant's preferred salts are those that may b added in sufficient concentrations such that vapor pressure

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is reduced by 5.0, 10, 20, 30, 40, 50, 100, 150, 200, 300 mm at initial boiling temperatures of fuel composition, by the addition of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0 grammolecules per liter. Preferred vapor pressure reductions are those greater than 20 mm, and preferred concentrations are less than 4.0, 3.0, 2.5, 2.0, 1.5, 1.0 grammolecules per liter.

Example 224

10 A fuel composition comprising a vapor pressure reducing amount of at least one salt soluble in hydrocarbon fuel or alternatively soluble in a co-solvent, wherein said salt can be treated at 0.5 grammolecules per liter of fuel, thereby reducing vapor pressure by at least 1.0, 2.0, 5.0, 15 7.5, 10.0, 15.0 mm at either ambient temperature or at vaporization temperatures of the fuel, whichever is higher.

Example 225

20 Method wherein treatment levels range from 0.001 to 30.0 grammolecules per liter (more preferred being 0.01 to 5.0 grammolecules per liter).

Example 226

25 The Example of 212-223, wherein said compositions additionally contain a vapor pressure reducing or flash point increasing amount of a salt.

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Rocket Fuel Applications

Rocket engine propulsion is a particularly desirable object of this invention and has been set forth in detail in my companion International Application No. 5 PCT/US95/02691, incorporated herewith by reference.

Example 227

A rocket fuel propellant comprising an ECS compound selected from the group of dimethyl carbonate, acetylen ,
10 aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, diborane, diethylenetriamine, ethane, ethanol, ethylamine, ethylene, ethylene diamine, ethylene oxide, ethyl nitrate, furfuryl alcohol, gasoline, heptene, hydrazine (including substituted hydrazines), hydrogen,
15 isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, methylamine, nitromethane, nitropropane, n-octane, propane, n-propyl nitrate, o-toluidine, triethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, 2,3-xylidene,
20 lithium borohydride, monomethylhydrazine, pentaborane, and mixture; and a propulsion improving amount of a metallic.

Example 228

The example of 180, wherein composition additionally
25 comprises a known oxidizer, selected from the group consisting of liquid oxygen, nitric acid, mixed nitric acid sulfuric acid combinations, fluorine, nitrogen tetroxide, hydrogen peroxide, potassium perchlorate, perchloryl

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fluoride, bromine pentafluoride, chlorine trifluoride, ON
7030, ozone, oxygen difluoride, RFNA (at various
strengths), WFNA, tetranitromethane, fluorine, chlorine
trifluoride, perchloryl fluoride, nitrosyl fluoride, nitryl
5 fluoride, nitrogen trifluoride, difluorine monoxide,
fluorate, chlorine oxides, and the like.

Example 229

A rocket fuel composition comprising hydrogen peroxide
10 and a metallic, such as cyclopentadienyl manganese
tricarbonyl compound, and optionally, DMC.

Example 230

A rocket fuel composition comprising hydrogen
15 peroxide, an oxidizer, a metallic, and optionally DMC.

Example 231

The rocket fuel composition of 230, wherein the metal
is selected from the group consisting of cyclopentadienyl
20 manganese tricarbonyl, technetium, rhenium, aluminum,
beryllium or boron compound, including pentaborane,
decaborane, borazole, aluminum borohydride,
trimethylaluminum, beryllium borohydride,
dimethylberyllium, lithium borohydride, homologues
25 thereof, and mixtures.

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Example 232

A rocket fuel for air breathing systems comprising dimethyl carbonate, a metallic; and optionally a rocket co-fuel; and optionally an oxidizer.

5

Example 233

Example 232, wherein non-limiting examples of a rocket co-fuel include hydrogen, hydrazine and kerosene.

10 Example 234

A rocket fuel composition comprising hydrogen peroxide, CMT, and a co-propellant selected from the group consisting of dimethyl carbonate, acetylene, aluminum borohydride, ammonia, aniline, benzene, butyl mercaptan, 15 diborane, diethylenetriamine, ethane, ethanol, ethylamine, ethylene, ethylene diamine, ethylene oxide, ethyl nitrate, furfuryl alcohol, gasoline, heptene, hydrazine (including substituted hydrazines), hydrogen, isopropyl alcohol, lithium, lithium hydride, methane, methylal, methanol, 20 methylamine, nitromethane, nitropropane, n-octane, propane, n-propyl nitrate, o-toluidine, triethylamine, trimethyl trithiophosphite, turpentine, unsymmetrical dimethyl hydrazine, 2,3-xylidene, lithium borohydride, monomethylhydrazine, pentaborane, and mixture; and a 25 propulsion improving amount of a cyclomatic manganese tricarbonyl compound.

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Example 235

A method for enhanced vapor phase combustion of a metallic, wherein said vapor is combusted in a rocket engine; and is derived from and ECS compound representing
5 0.01% to 50% oxygen by wt in the fuel, a metallic representing 0.01 to 1000.0 grs of metal/gal, and optionally a co-propellant and/or oxidizer.

Those skilled in the art will appreciate that many
10 variations and modifications of the invention disclosed herein may be made without departing from the spirit and scope thereof.

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Thus having disclosed my invention, I claim:

1) A method of reduced temperature metallic vapor phase combustion, said method comprising: vaporizing or injecting a fuel of a particle size not exceeding an average of 70 microns under suitable pressure into an air breathing combustion system; said fuel vapor solely comprised of at least one fuel soluble non-leaded metallic whose oxide's heat of formation is negative and exceeds about -200,000 gr calories/mole, and at least one ECS compound having latent heat of evaporation exceeding about 200 btu/lb @ 60°F and a laminar burning velocity exceeding 48 cm/sec; introducing sufficient temperature to the vapor to cause ignition, whereinafter unburned vapor decomposes into reactive high kinetic energy free radicals; diffusing said radicals ahead of the flame front containing said metallic; whereupon combustion luminous vapor phase burning occurs.

2) The method of 1, wherein the ECS compound is oxygenated with a latent heat of vaporization exceeding about 31 kJ mol⁻¹ at its boiling temperature, not exceeding about 110°C.

3) The method claim 1), wherein the metallic vapor is derived from a metal or metallic compound selected from the group consisting of aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybden, nickel, niobium, phosphorus, potassium, pallium, rubibidium, sodium, tin,

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zinc, praseodymium, rhenium, salane, vanadium, and mixture; said metallic optionally having a heating value exceeding 9,500 Kcal/kg.

4) The method of 1, wherein the pre-combustion vapor is a product derived from dimethyl carbonate and an organo cyclomatic manganese compound and wherein the ratio of dimethyl carbonate to manganese compound is less than 2,500 parts to one.

5) The method of 1, wherein the pre-combustion vapor is a product derived from dimethyl carbonate, and a metal or a metal based product, selected from boron, magnesium, manganese, lithium, potassium, iodine, or mixture.

6) The method 1 or 4, wherein the pre-ignition vapor additionally comprises a vapor derived from a co-fuel selected from the group consisting of alternative fuel, hydrogen, petroleum gas, liquefied petroleum gas, LPG-propane, LPG-butane, natural gas, natural gas liquids, methane, ethane, propane, n-butane, propane-butane mixture, fuel methanol, e.g. M 80, M 90, or M 85 fuels, fuel ethanol, biomass fuels, vegetable oil/ester fuels, rap seed methyl ester, soybean fatty acid esters, aqueous carboneous fuels (including aqueous gasolines and diesels, e.g. Gunnerman A-55/D-55), automotive gasolines (meeting ASTM standards) aviation gasoline fuels, including grade 80, grade 100, grade 10011 (meeting ASTM standards), conventional automotive gasolines, reformulated gasolines (meeting U.S. Clean Air Act § 211 (k), California Air Resources Board, Swedish/European EPEFET standards), low

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vapor pressure gasolines, low sulfur/no-sulfur gasolines, low octane gasolines, Talbert E-gasolines, alkylate or substantially alkylate fuels (including aviation and automotive gasolines), reformat fuels, substantially reformat fuels, isooctane fuels, substantially isooctane fuels, paraffinic fuels, substantially paraffinic fuels (including optionally n-butane, isopentane, toluene, c7-c10 olefins), kerosine, wide range boiling fuels, gas turbine fuels, including No.0-GT, No.1-GT, No.2-GT, No.3-GT, No.4-GT (meeting ASTM standards), aviation jet turbine fuels including JP-4, JP-5, JP-7, JP-8, JP-9, JP-10, TS, Jet A-1, Jet A, Jet B (meeting ASTM standards), military aviation gasolines, missile fuels, solid and liquid rocket fuels, monopropellant, multipropellant fuels, hypergolic fuels, gas oil turbine-engine fuels, including grades 0-4, stratified-charged engine fuels, diesel fuels, including Grade low sulfur No. 1-D, Grade low sulfur No. 2-D, Grade No. 1-D, Grade No. 2-D, and Grade No 4-D (meeting ASTM standards), and older grades Type C-B, Type T-T, Type R-R, Type S-M, reformulated diesel fuels (meeting CARB or Swedish standards), low/no sulfur hydrotreated low/no aromatic distillate fuels, toluene fuels, substantially toluene fuels, naptha fuels, substantially naptha fuels, fuel oils, including Grade 1, Grade 2, Grade 4 (light), Grade 4, Grade 5 (light), Grade 5 (heavy), Grade 6, heavy diesel fuels for marine or railroad (meeting ASTM standards), including those complying with ISO DIS 8217 and BS MA 100 standards, various distillate oils, distillate

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fuels, substantially distillate fuels, residual type oils, cycle oils, light cycle oils, light cycle gas oils, heavy cycle oils, heating oils, heavy cycle gas oils, vacuum oils, burner oils, furnace oils, coal liquids, SRC-II middle distillate coal fuels, near coal liquids, powdered coal, coal derivatives, coal, solid fuels, tar sand fuels, shale oil fuels, hydrazine, ammonia acetylene, and/or any fuel meeting ASTM specifications, EPA certification standards, CARB or Swedish European standard, or meeting any industry and/or any government specification or regulation, present and future, including mixtures thereof; said fuel vapor optionally containing low concentrations of sulfur or no sulfur and/or low amounts or no phosphorus; said co-fuel vapor characterised as representing substantial majority, majority, substantial minority or minority of the precombustion vapor.

7) The method of 6, wherein said pre-combustion vapor is derived from a ECS/co-fuel combination; said combination characterized as meeting all ASTM, government, and industry specifications and standards of said co-fuel, including minimum distillation temperature, flash point, additive, vapor pressure, composition ranges, ingredients, emissions, heats of combustion, and those other set forth in the specification.

8) The method of 7, wherein latent heat of vaporization of said co-fuel is increased to an amount greater than 1.5% of the unadjusted co-fuel prior to its combination with ECS fuel.

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9) The method of claim 1 or 6, wherein said vapor additionally comprises at least one additive or detergent, selected from additives which control combustion chamber deposits, valve intake deposits, fuel injector deposits, or
5 other additive as set forth in the specification.

10) The method of 1 or 6, wherein the combustion of said vapor powers a large engine exceeding 6.5 liters (400 cubic inch) displacement (or equivalent) operated under heavy load; whereby combustion temperatures are reduced and
10 fuel economy is improved over co-fuel operation alone.

11) The method of claim 1 or 6, wherein said vapor is combusted in an engine or combustor selected from group consisting of rocket engine, Brayton cycle engine, gas oil turbine, aviation jet turbine, diesel engine (including
15 direct injection, turbo charge, lean burn, swirl, variable valve timing and lift), marine, locomotive, aviation gas engine, gasoline/automotive engine (including low emission, ultra low emission, variable-valve timing and lift, direct fuel injection, three-way catalyst systems, lean burn
20 engines), oil burner, residue burner, oil furnace, gas burner, gas furnace, internal compression engine, spark-ignited internal combustion engine, lean burn, fast burn, external combustion Stirling or Rankine engine, Otto cycle engine, Miller cycle, two stroke, four stroke, or catalyst
25 system; whereby the thermal or combustion efficiency of said engine operation is increased over usage of co-fuel alone.

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12) The method of 11, wherein said combustion system comprises mechanical means for reducing combustion temperatures and/or increasing burning velocity; characterized as increasing fuel economy, burning velocity and/or reducing combustion temperature of ECS based fuel, greater than an amount attributable to said fuel alone in unmodified system.

13) The method of claim 12, wherein mechanical means includes use of at least one system selected from the group consisting of advanced evaporators, combustor designs enhancing combustion turbulence, swirl or high swirl combustors or chambers, spherical combustors, divided chambers, engine design maximizing increased power combustion pressure (pressure densities), engine design maximizing lower combustion temperatures, lean burn systems, catalytic combustors/combustion systems, pre-mixed combustor, diffusion flame combustors, lean premixed pre-evaporizing combustor, pre-evaporizing premixing combustor, variable compression ratio engines, indirect injection methods, direct injection methods, direct injection stratified charge engines, three-way catalytic systems, high swirl ratio to lean-air ratio systems (particularly during ignition to warm up), variable-valve timing technology (including computer enhancement), turbochargers, port fuel injection systems, tuned intake and exhaust, multiple valves, knock sensors, oxygen sensors, electronic feed-back control, adaptive learning computer enhanced systems, re-entrant combustion chambers, pre-

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combustion chambers, re-matched inlet port swirl systems, reduced quenching systems, reduced heat transfer systems, enhanced fuel-air mixing systems (including computer enhanced systems), enhanced spray atomizer kinetic energy systems, injector designs enhancing fuel-air mixing, water injection systems, computer enhanced systems, fuel-air adjustment system (including computer enhance systems), lean-burn and/or fast burn combustion systems, tumble air motion systems, four valve pent roof combustion chambers, indirect injection combustors or chambers, indirect injection swirl combustors or chambers, direct injection combustors or chambers, turbulence enhancing combustor or chambers, advanced cooling, after-cooling systems, coolant systems or air intake systems reducing inlet air temperatures, fuel injection systems (especially those capable of directing a fine uniform atomized spray of vapors at enhanced dynamic flow rates and pressures at desirable angles into combustion chambers, combustors, and burners), and/or other mechanical means, including additional means set forth in the specification;

14) The method of 1 and 11, wherein the vapor additional comprises an oxidizer.

15) The method of Claim 7 or 11, wherein said vapor is combusted in a jet turbine combustor; and is derived from DMC representing 0.01% to 40.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to 20.0 gr/gal, an aviation jet turbine co-fuel base; wherein combined fuel is characterized as having a total aromatic

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volume concentration not exceeding 25% or 22%, a maximum sulfur content not exceeding 0.3, 0.2, 0.1 weight percent or sulfur free, a maximum T-10 temperature of 205°C, a maximum final boiling point temperature of 300°C, 280°C, or 260°C, a minimum flash point of 38°C, a density range of about 751 to 840 at 15°C, kg/m³, a minimum freezing point of -40°C, -5°C, or -57°C, a minimum net heat of combustion of 42.8 KJ/kg, a minimum latent heat of vaporization of 115 BTU/lb; whereby combined fuel meets ASTM 1655 finished fuel requirements for either Jet A, Jet A-1, or Jet B; whereby said method is characterized as increasing the lift and/or operating range of jet compared to aviation co-fuel alone.

16) The method of claim 15, wherein combustion occurs at an altitude in excess of 10,000 feet above sea level, whereby thermal, combustion efficiency or lift is improved over co-fuel alone.

17) The method of Claim 15 and 16, wherein inlet turbine temperature and pressure, and turbine outlet pressure operate jet in excess of mach 3, 4, 5, or 6.

18) The method of Claim 7 or 11, wherein said vapor is combusted in a diesel engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 2.5 gr/gal, a diesel co-fuel base; wherein combined fuel is characterized as having density ranging from about 880 to 800 kg/m³; viscosity ranging from 2.5 to 1.0 cSt at 40°C; cetane index of 40 to 70; an aromatic content by vol. ranging from approximately 0 to 35%, 0% to 20.0%, 0% to

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15%, or 0% to 10% (inclusive 3-ring + aromatics not to exceed 0.16 vol%); a T10 fraction temperature of about 190 to 230°C, a T50 fraction temperature of about 220 to 280°C, and a T90 fraction of about 260 to 340°C, and cloud point temperature of °C -10, -28, -32 (or 6°C above tenth percentile minimum ambient temperature); optionally a sulfur content not greater than 250 ppm, 200 ppm, 100 ppm, 50 ppm, 40 ppm, 30 ppm, 20 ppm, 5 ppm, or being sulfur free; a bunsen laminar burning velocity of at least 40 cm/sec, a latent heat of vaporization of at least 110 BTU/lb; said method characterized in achieving reduced particulate emissions or improved fuel economy compared to co-fuel alone.

19) The method of Claim 7 or 11, wherein said vapor is combusted in a diesel engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 2.5 gr/gal, a diesel co-fuel base; wherein combined fuel is characterized as having an API range of about 41.1 to 45.4, optionally a sulfur content not exceeding 300, 250, 200, 150, 100, 50, 40, 20, 10, 5 wt ppm or sulfur free, absent nitrogen, and an aromatic content ranging from 0 to 5%, 1 to 10%, 0 to 15%, 0 to 20%, 0 to 35% by volume, PNA vol% of 0.03, 0.02, or less, a Cetane index greater than 45, an IBP of approximately 365°F, a 95% fraction ranging from 460°F to 540°F; a bunsen laminar burning velocity of at least 38 cm/sec, a latent heat of vaporization of at least 105 BTU/lb; said method characterized in achieving reduced

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particulate emissions or improved fuel economy compared to co-fuel alone.

20) The method of Claim 7 or 11, wherein said vapor is combusted in a aviation gasoline engine; and is derived from DMC representing 0.01% to 10.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 2.5 gr/gal, an aviation gasoline co-fuel; wherein combined fuel is characterised as having a minimum knock octane number of 80, or 100 and minimum performance number of 87, or 130, optionally containing lead, a max T10 distillation temperature of 75°C, a minimum T40 temperture of 75°C, a maximum T50 temperature of 105°C, a maximum T90 temperature of 135°C, a maximum end temperature of 135°C, where the sum of the T10 and T50 temperatures is a minimum of 135°C, a maximum sulfur content of 0.05 wt%, optionally a minimum net heat of combustion of 18,720 BTU/lb, a latent heat of vaporization exceeding 140, 150, 155, or 160 BTU/lb; whereby when combusted in said aviation engine at altitude of at least 5,000 feet above ground level combustion completeness or thermal efficiency is greater than unadjusted aviation co-fuel alone.

21) The method of claim 7 or 11, wherein said vapor is combusted in an aviation gasoline engine; and is derived from an ECS compound representing 0.01% to 15.0% oxygen by weight of a fuel, an organo manganese representing about 0.001 to 3.0 gr Mn/gal of fuel, and an ASTM or other aviation co-fuel having a minimum heat of combustion of 18,720 BTU/lb; whereby said combined fuel has heat of

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combustion lower than 18,720 BTU/lb due to dilution effect of DMC; said method characterized in that aviation engine combusting lower heat of combustion vapor has increased flight range compared to higher heat of combustion vapors from co-fuel alone.

22) The method of Claim 7 or 11, wherein said vapor is combusted in a gas oil turbine combustor; and is derived from DMC representing 0.01% to 40.0% oxygen by wt in the fuel, at least one metallic in a concentration of 0.001 to about 7.5 gr/gal, and a gas oil turbine co-fuel selected from No. 0-GT, No. 1-GT, No. 2-GT, No. 3-GT or No. 4-GT gas turbine fuel oil, or other oil; wherein combined fuel is characterized as having a minimum flash point of 38°C to 66°C, a minimum kinetic viscosity at 40°C ranging from 1.3 to 5.5 2mm/s (ASTM D 445), optionally a sulfur content not exceeding 1500, 500, 400, 300, 200, 100, 50, 40, 20 ppm wt (or being sulfur free), optionally a reduced T90 temperature of at least 20°C, a bunsen laminar burning velocity of at least 35, 36 cm/sec, a latent heat of vaporization of at least 100 BTU/lb; whereby turbine inlet gas temperature is less than 650°C, 600°C, or 550°C and/or whereby inlet pressure is increased compared to co-fuel alone.

23) The method of Claim 15 or 22, wherein said combustor's flame tube has a dilution zone length of approximately 1.4 to 1.6 times the total flame tube width.

24) The method of Claims 1, 4, 5, 6, 7, 15, 18, 19, 20, 21, or 22 wherein a co-solvent or co-solvent mixture,

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and/or salt is employed to increase flash point or reduce vapor pressure.

25) A composition of matter comprising at least one ECS compound having a latent heat of evaporation exceeding
5 200 btu/lb @ 60°F and a laminar burning velocity exceeding 48 cm/sec, and a combustion improving amount of at least one fuel soluble high heating value non-leaded metallic whose oxide's heat of formation is negative and exceeds about -200,000 gr calories/mole, said metal or metallic
10 containing compound, is selected from the metals consisting of aluminum, boron, bromine, bismuth, beryllium, calcium, cesium, chromium, cobalt, copper, francium, gallium, germanium, iodine, iron, indium, lithium, magnesium, manganese, molybden, nickel, niobium, phosphorus,
15 potassium, pallium, rubibidium, sodium, tin, zinc, praseodymium, rhenium, salane, vanadium, and mixture.

26) The composition of claim 25, additionally comprising a majority, substantial minority, or minority of at least one co-fuel; said combination characterized as
20 having latent heat of vaporization and burning velocity greater than co-fuel alone; whereby thermal efficiency or combustion temperature of combined fuel is superior to co-fuel alone.

27) The composition of Claims 25, 26, additionally comprising a co-solvent or co-solvent mixture, and/or salt; whereby addition increases flash point or reduces vapor
25 pressure of the composition.

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28) The method of Claim 7 or 11, wherein said vapor is combusted in a gasoline automotive engine; and is derived from DMC representing 0.01% to 3.5% oxygen by wt in the fuel, at least one metallic in a concentration up to 1/64, 1/32, 1/16, 1/8, 1/4 or 3/8 gr/gal, and a conventional or reformulated gasoline co-fuel; said combined fuel characterized as having a sulfur content less than 300, 200, 100, 20, or 10 ppm (including sulfur free); a polynuclear free aromatic concentration of less than 35%, 27%, 20%, 15%, 10% (including aromatic free); an olefin concentration (excluding C4-C5 olefins) less than 15%, 10%, 8%, 5%, (or olefin free); a benzene concentration of less than 1.0%, 0.9%, 0.8%, 0.7% volume (or benzene free); an RVP of less than 10.0, 8.5, 8.0, 7.5, 6.9, 6.5, 6.0 psi, or less; a minimum octane (R+M)/2 of 93, 92, 91, 90, 89, 88, 87, 86, 85; at least one deposit control additive selected from combustion chamber deposit control, port fuel injector, or intake valve deposit control additive; a driveability index less than 1120, 960, or 930 (preferred); optionally a t-50 temperature greater than 170°F, a T-10 temperature less than 140°F, 120°F; a heat of vaporization equal to or greater than 140, 145, 150, 152, 155 btu/lb; optionally a minimum laminar burning velocity of 48, 49 cm/sec.

29) The method of Claim 7 or 11, wherein said vapor is combusted in a heavy diesel, locomotive or marine engine; and is derived from DMC representing 0.01% to 40% oxygen by wt in the fuel, a metallic representing 0.01 to

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20.0 grs of metal/gal, and a heavy diesel, locomotive or marine engine co-fuel meeting ISO DIS 8217 and/or BS MA 100 standards specifications; wherein said combination contains a sulfur concentration of 0.01 to 3.0% mass, has a viscosity of 10 to 500 centistokes at 50°C; whereby combustion of said vapors in said engine results in reduced corrosion, particulate emissions and/or improved fuel consumption compared to co-fuel alone.

30) The method of 29, wherein operation of said heavy diesel, locomotive or marine engine is load and whereby fuel consumption is improved by at least 0.5% to 5.0%, over co-fuel alone.

31) The method of Claim 7 or 11, wherein said vapor is combusted in a rocket engine; and is derived from and ECS compound representing 0.01% to 50% oxygen by wt in the fuel, a metallic representing 0.01 to 1000.0 grs of metal/gal, and optionally a co-propellant and optionally an oxidizer.

32) A method of increasing work potential, fuel economy, or reducing emissions of a gasoline vehicle operating on conventional or reformulated gasoline, comprising: Reducing the boiling temperature of gasoline such that its T-90 fraction is no greater than 300°F, increasing its latent heat of vaporization above 155 btu/lb; optionally admixing MMT up to 1/64, 1/32 gr mn/gal; combusting said composition in a gasoline powered vehicle; whereby fuel economy is improved over unadjusted fuel.

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33) A fuel composition comprising a conventional or reformulated gasoline, oxygenate optional; said composition characterized as having a T-90 fraction no greater than 300°F, 290°F, 280°F, a minimum latent heat of vaporization of 155, 160, 165 btu/lb; optionally a burning velocity exceeding 49, 50, 51 cm/sec, optionally at least one cyclomatic manganese tricarbonyl up to 1/64, 1/32 gr mn/gal.

34) A fuel composition comprising: an ECS compound, optionally a combustion improving amount of a metallic, a co-fuel, a co-solvent; wherein said composition conforms to minimum ASTM or industry vapor pressure or flash point standards.

35) An ameliorative fuel composition characterized as an aviation/automotive gasoline, diesel, turbine, fuel oil, or other fuel containing MTBE, ETBE, TAME, or mixture; said fuel additionally containing a combustion improving amount of an ECS compound (preferably DMC) having a burning velocity and/or a latent heat of vaporization greater than MTBE; and optionally a combustion improving amount of at least one metallic; whereby enhanced attributes of combustion accelerate decomposition of carcinogenic ether prior to its emission into atmosphere.

36) A composition of matter comprising; an unleaded conventional or reformulated gasoline composition conforming with Clean Air Act requirements under § 211(k), said composition additionally characterized as having a minimum latent heat of vaporization of about 153, 154

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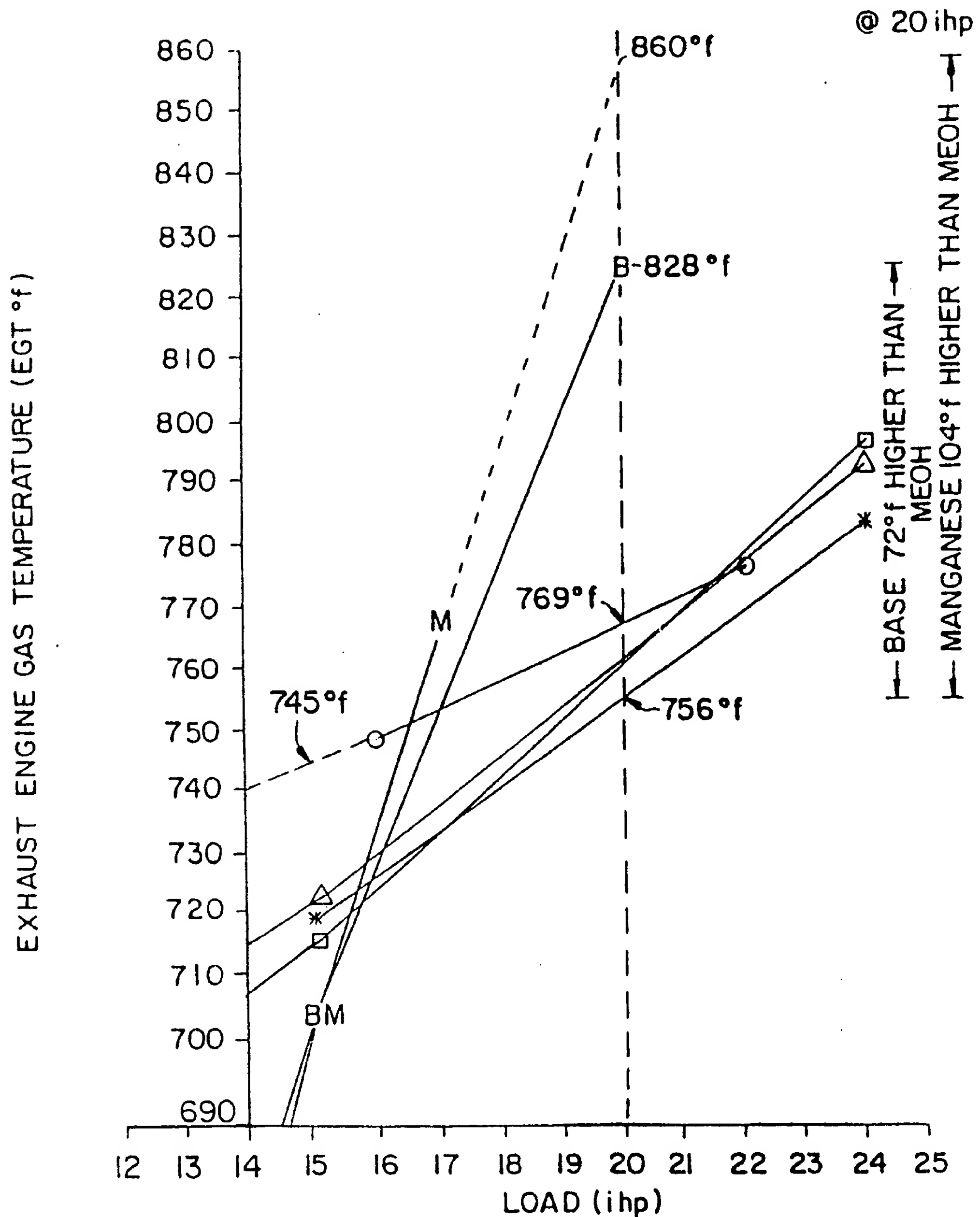
btu/lb @ 60°F, and optionally a minimum laminar flame burning velocity of 49, 50, 51 cm/sec.

37) A method of avoiding CCD deposits employing an ECS/co-fuel combination, said method comprising: mixing a
5 co-fuel with combustion improving amount of a metallic and a ECS compound (preferably DMC); a combustion chamber deposit (CCD) control additive; and a co-fuel; combusting said fuel in an engine for the equivalent of 5,000, 10,000, 15,000, 20,000, 30,000, 50,000, 75,000, or 100,000 miles;
10 wherein the octane requirement for engine operating on ECS/co-fuel combination does not exceed, or is less, than the octane requirement of same engine operating on clear co-fuel alone (but containing same CCD additive).

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FIG. 1 (TEST TWO)

COMBUSTION TEMPERATURE DIFFERENCES



B - BASE FUEL
M - MANGANESE FUEL
O - MTBE FUEL
□ - DMC FUEL
△ - METHYLAL FUEL
* - MEOH FUEL

SUBSTITUTE SHEET (RULE 26)

FIG.2 (TEST TWO)
COMBUSTION TEMPERATURES AND HYDROCARBON EMISSIONS

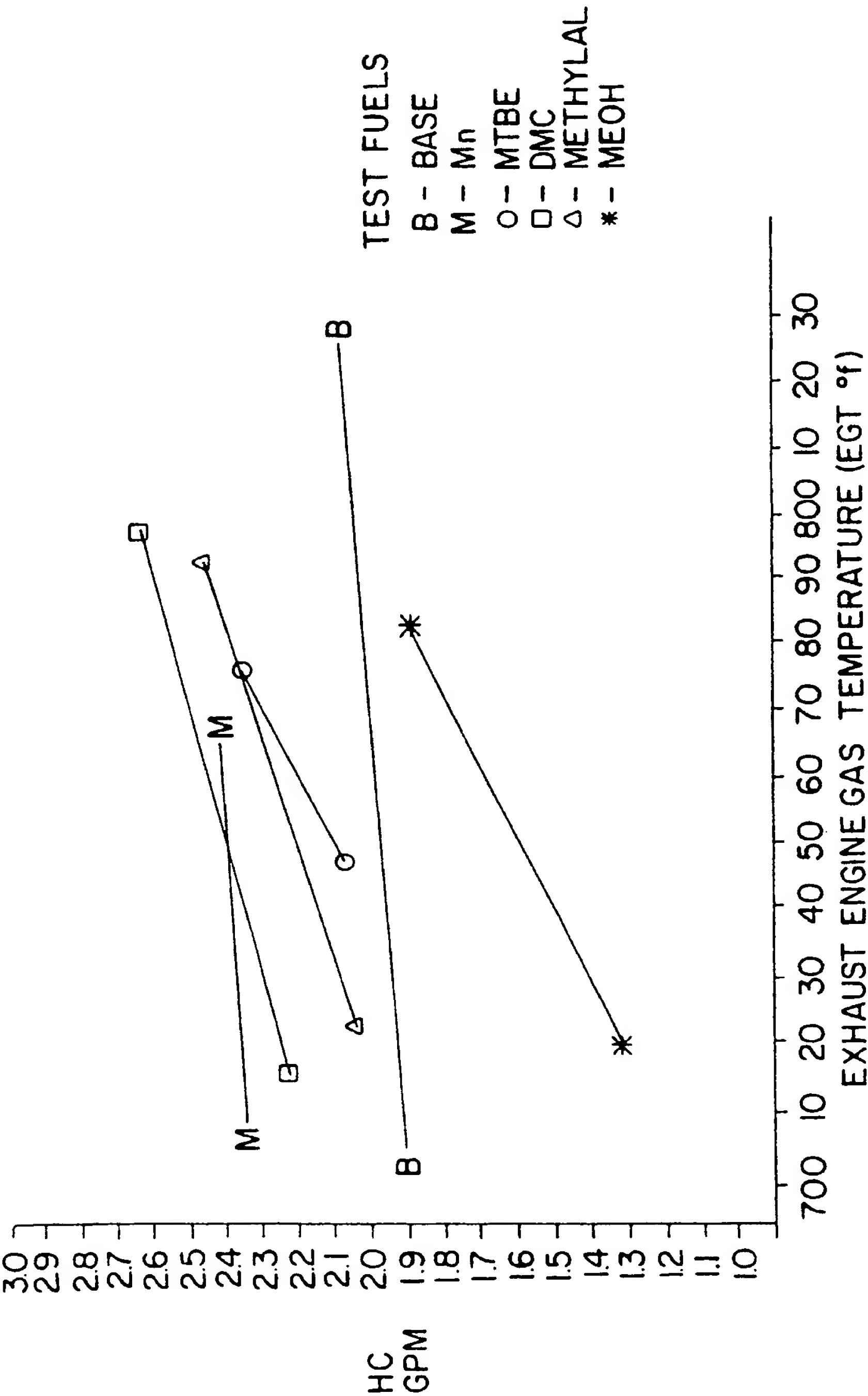
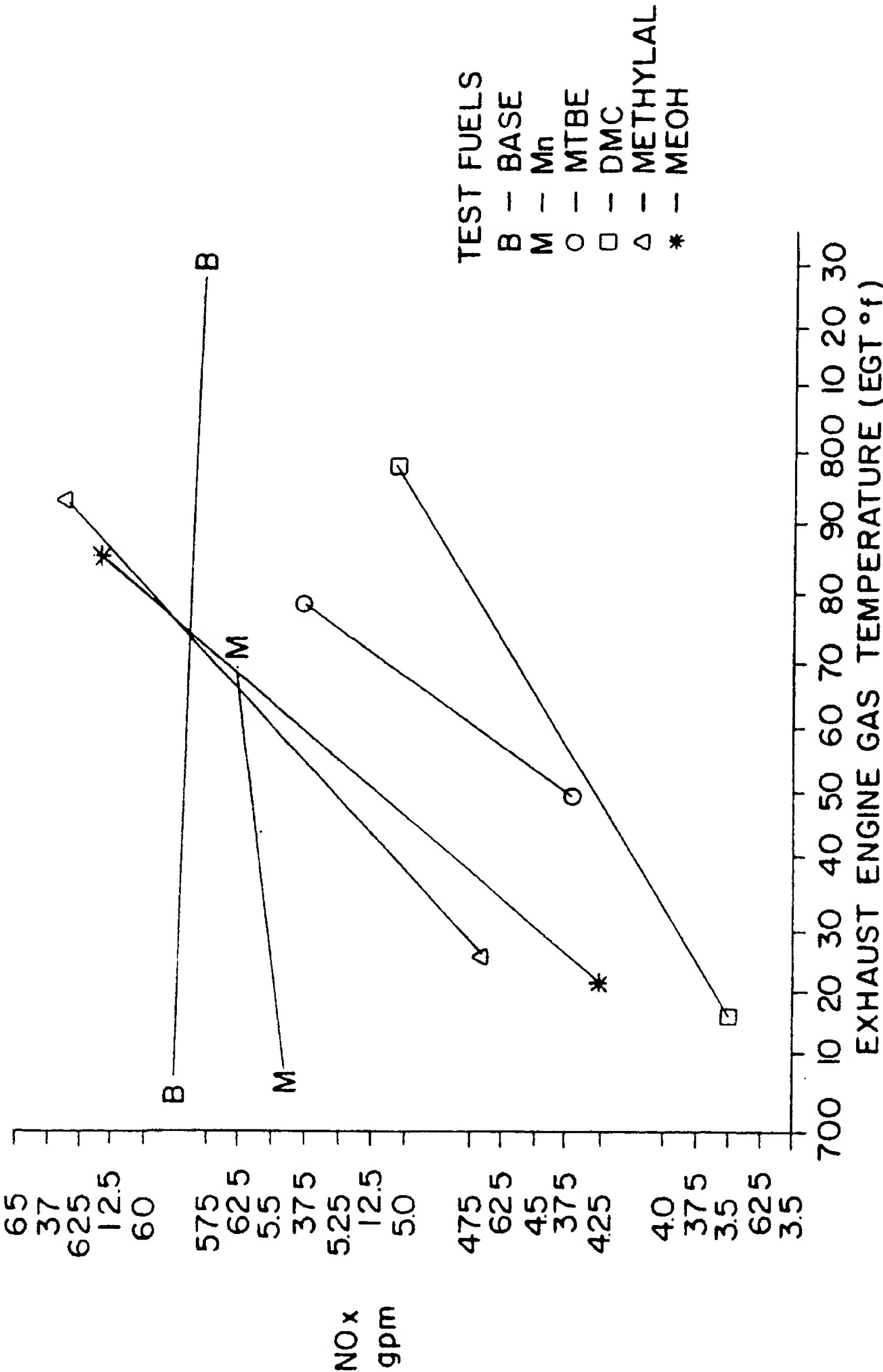


FIG.3 (TEST TWO)
COMBUSTION TEMPERATURES AND NOx EMISSIONS



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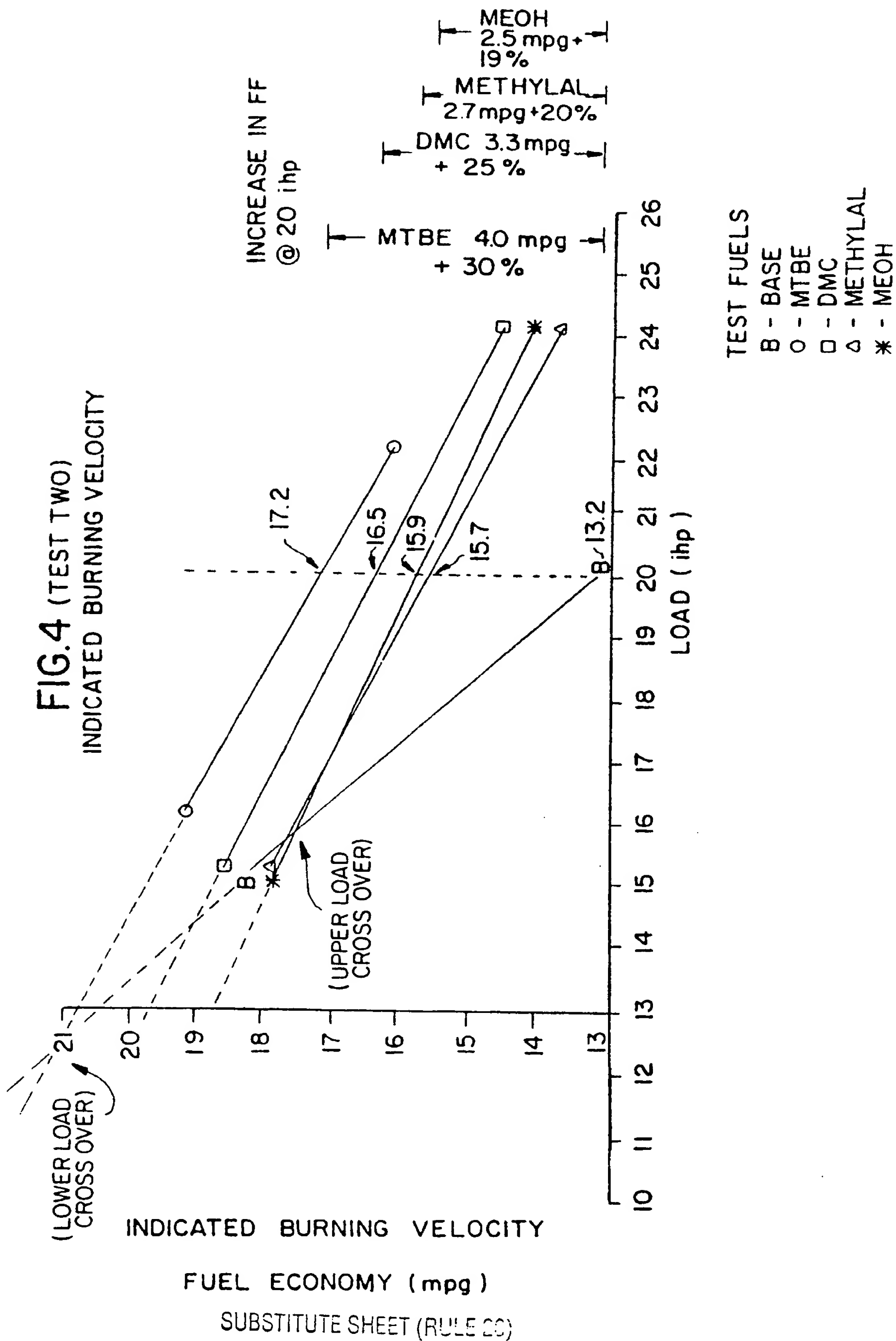
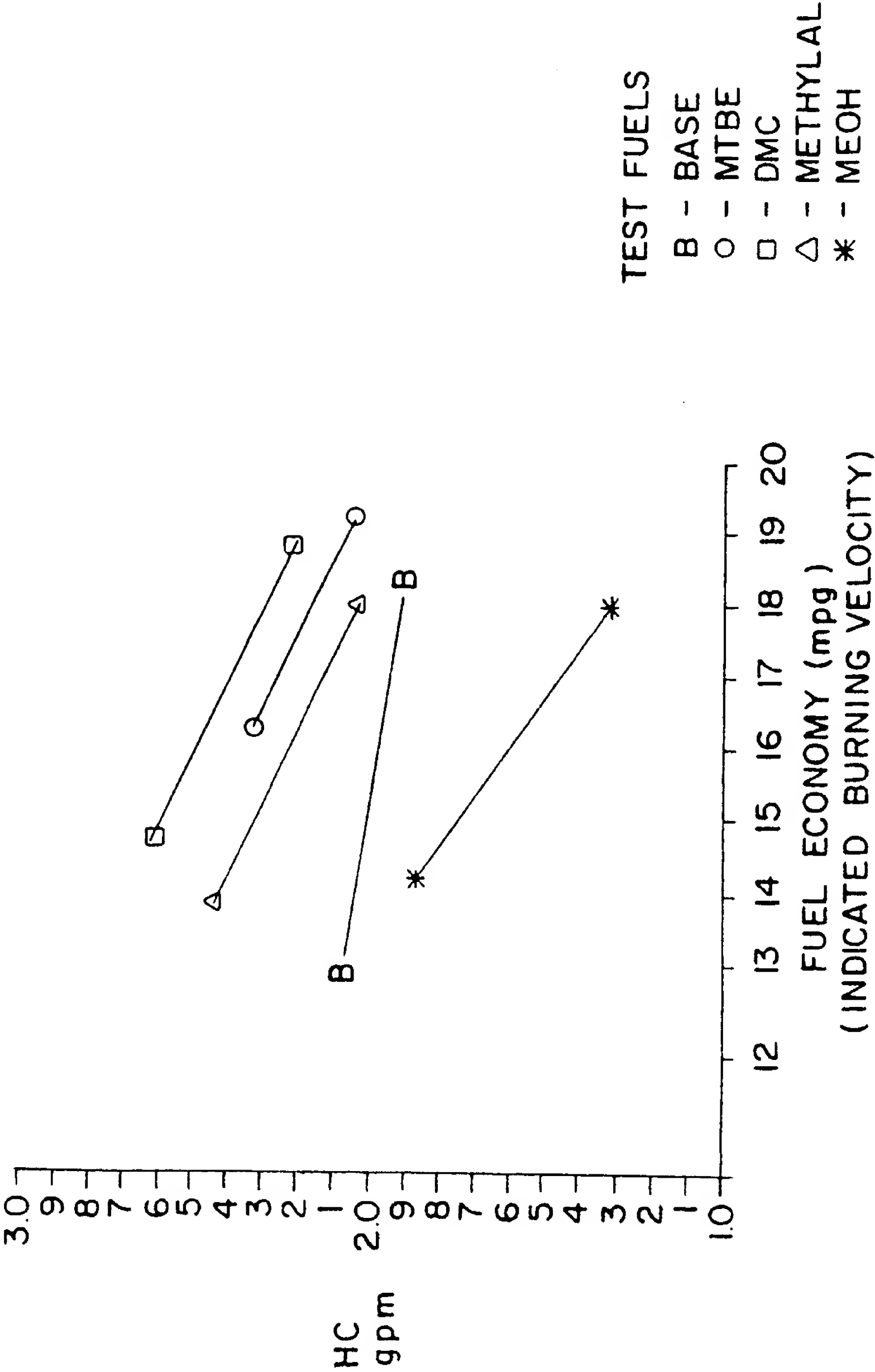
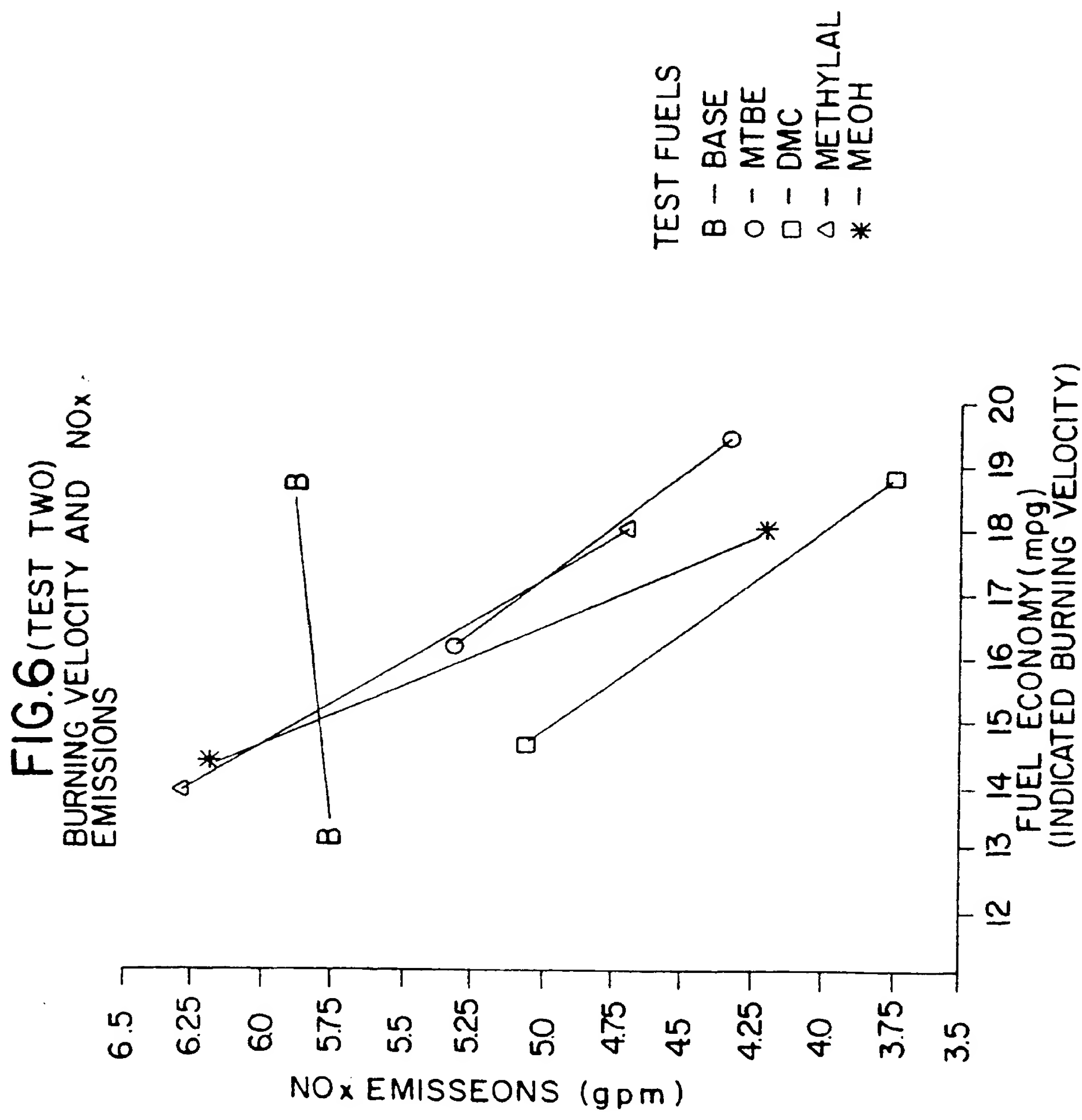


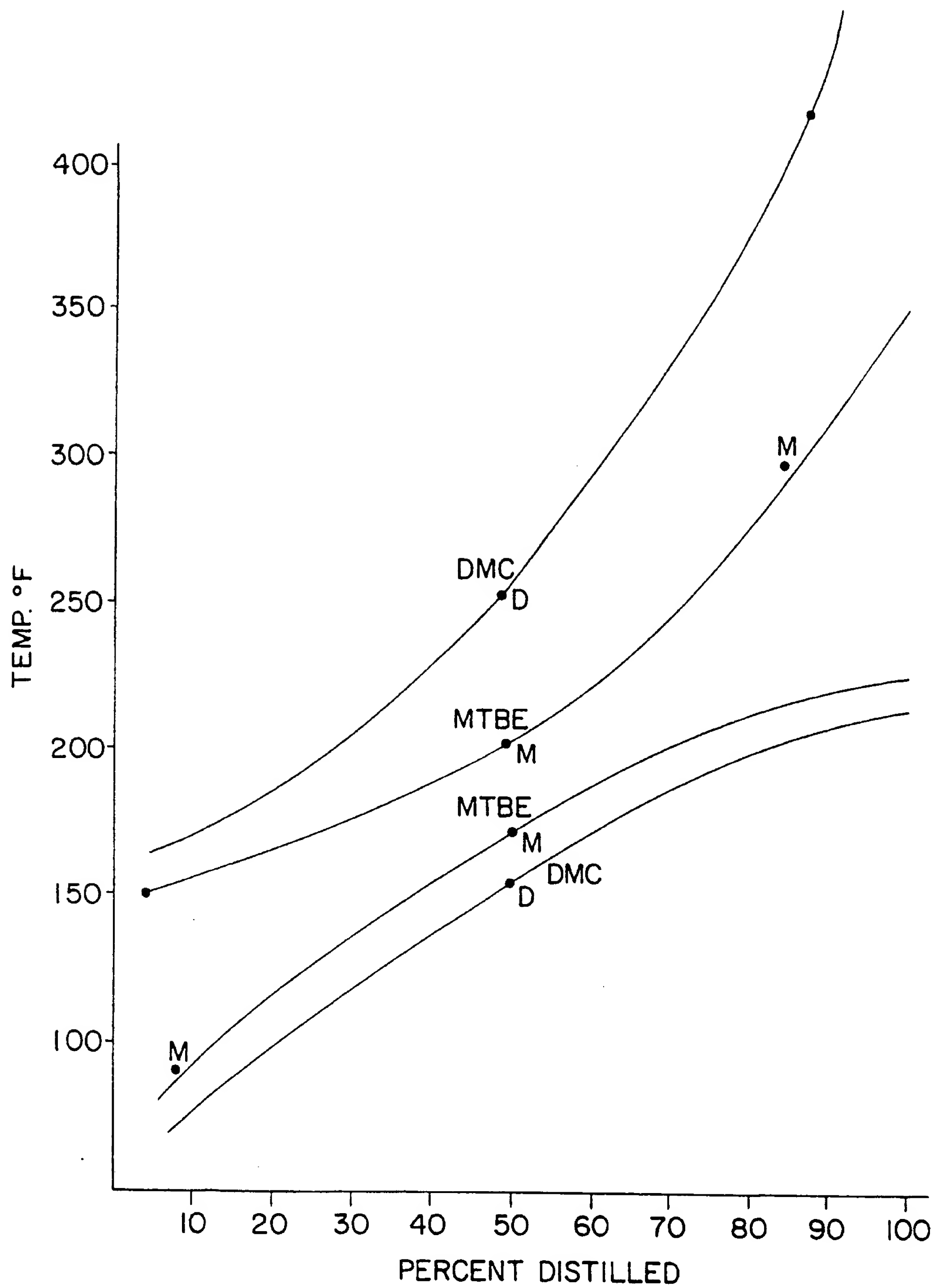
FIG. 5 (TEST TWO)
BURNING VELOCITY AND HC EMISSIONS





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FIG. 7



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/06758

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3946057	23-03-76	NONE	
EP-A-112219	27-06-84	FR-A- 2537593	15-06-84
		JP-C- 1636693	31-01-92
		JP-B- 2056396	30-11-90
		JP-A- 59172592	29-09-84
		US-A- 4568360	04-02-86
WO-A-8700193	15-01-87	AU-A- 5963286	30-01-87
		EP-A- 0229089	22-07-87
		JP-T- 62503173	17-12-87

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/06758

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9404636	03-03-94	AU-B- 5089593 CA-A- 2142991 EP-A- 0656045	15-03-94 03-03-94 07-06-95
EP-A-476196	25-03-92	AU-B- 635158 AU-A- 8465091 CA-A- 2051452 DE-D- 69004692 DE-T- 69004692 JP-A- 4234489	11-03-93 26-03-92 21-03-92 23-12-93 10-03-94 24-08-92
US-A-3883320	13-05-75	NONE	
EP-A-540297	05-05-93	AU-B- 656237 AU-A- 2724992 CA-A- 2080193 JP-A- 5239477	27-01-95 29-04-93 29-04-93 17-09-93
EP-A-609089	03-08-94	AU-B- 6167294 CA-A- 2114499 WO-A- 9417158	15-08-94 30-07-94 04-08-94
EP-A-435631	03-07-91	GB-A- 2239258 DE-D- 69006588 DE-T- 69006588 JP-A- 4114090	26-06-91 24-03-94 26-05-94 15-04-92
WO-A-8701384	12-03-87	AU-A- 6377586 DE-A- 3682503 EP-A, B 0235280	24-03-87 19-12-91 09-09-87
EP-A-466511	15-01-92	AU-B- 648564 AU-A- 8016791 CA-A- 2045455 DE-D- 69106611 DE-T- 69106611 ES-T- 2066357 JP-A- 4226598	28-04-94 16-01-92 14-01-92 23-02-95 18-05-95 01-03-95 17-08-92
US-A-4207078	10-06-80	NONE	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/06758

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	EP,A,0 609 089 (ETHYL) 3 August 1994 see the whole document ---	20,21,24
Y	EP,A,0 435 631 (ETHYL) 3 July 1991 see the whole document ---	29,30
X	WO,A,87 01384 (ORR,W.) 12 March 1987 see the whole document ---	1-3, 6-14, 25-28, 32-37
X	EP,A,0 466 511 (ETHYL) 15 January 1992 see the whole document ---	1-3,6-9, 11,14, 25-28, 32-37
X	US,A,4 207 078 (SWEENEY ET AL.) 10 June 1980 cited in the application see the whole document ---	1-3,6-9, 11,14, 25-28, 32-37
A	US,A,3 946 057 (REEDY) 23 March 1976 see column 4, line 56 - line 58 ---	31
A	EP,A,0 112 219 (COMPAGNIE FRANCAISE DE RAFFINAGE ET AL.) 27 June 1984 see the whole document ---	1-37
A	WO,A,87 00193 (SPAROL) 15 January 1987 see the whole document -----	1-37

INTERNATIONAL SEARCH REPORT

In International Application No

PCT/US 95/06758

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L1/14 C10L10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,94 04636 (ORR,W.) 3 March 1994	1-14, 25-28, 32-37
Y	see the whole document	15-24, 29,30
Y	EP,A,0 476 196 (ETHYL) 25 March 1992 see page 9, line 28 - line 35	15-24, 29,30
Y	US,A,3 883 320 (STRUKL) 13 May 1975 see the whole document	15-17, 23,24
Y	EP,A,0 540 297 (ETHYL) 5 May 1993 see the whole document	20,21,24

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

24 August 1995

Date of mailing of the international search report

01-09-1995

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